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THE VELOCITY OF THERMAL DECOMPOSITION

of

OXALACETIC ESTER DERIVATIVES,

and

THE THEORY OF UNIMOLECULAR REACTIONS.

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by

DAVID LINDSAY WATSON.

I N D E X.

PART I.

THE VELOCITY OF THERMAL DECOMPOSITION OF OXALACETIC ESTER DERIVATIVES.

INTRODUCTORY.

It is well known that it is possible to obtain carbon monoxide, by heating oxalic acid over 100°C :

$$COOH.\ COOH \longrightarrow CO + CO_2 + H_2O \qquad (1)$$

though formic acid may also be produced:

$$COOH.\ COOH \longrightarrow H.\ COOH + CO_2 \ . \qquad (2)$$

By esterifying one of the hydrogens of oxalic acid, we obtain a compound, which dissociates according to equation (2):

$$COOH.\ COOC_2H_5 \longrightarrow H.COOC_2H_5 + CO_2,$$

while, by the addition of concentrated sulphuric acid, we can make the reaction follow the first course. It is not so well known, however, that it is possible to obtain derivatives of oxalic ester which on heating, yield carbon monoxide alone. Wislicenus noticed in 1894 (Ber. 27, 792), that certain derivatives of oxalacetic ester, when heated to 150° - 200°, gave a quantitative yield of carbon monoxide - Eg.

$$COOC_2H_5.CO.CHR.COOC_2H_5 \longrightarrow CO + COOC_2H_5.CHR.COOC_2H_5 \qquad (3)$$

- a derivative of malonic ester being simultaneously produced.

Such/

Such compounds can be prepared by condensing diethyl oxalate with an acetic ester derivative, in the presence of dried sodium ethylate:

$$\begin{aligned} &COOEt.\ COOEt + \\ &CH_2R.\ COO\text{-}Et \\ &+ NaO\text{-}Et. \end{aligned} \quad = \quad \begin{aligned} &COOEt.C(ONa) : CR.COO\text{-}Et \\ &+ 2\ Et\text{-}OH. \end{aligned} \qquad (4)$$

The thermal decomposition (3) was given the name of "Kohlenoxydspaltung" by Wislicenus and it was the first object of this research to examine the kinetics of this peculiar reaction, in which a carbon atom actually seems to break from the middle of a chain.

For this purpose, the ethoxy derivative, ethoxy oxalacetic (diethyl) ester, was chosen (COO-Et.CO.CH(OEt). COOEt), and it was soon established that, at a temperature near 185°C, the decomposition followed the unimolecular law:

$$k = \frac{1}{t} \log {}^{a}/_{a-x} \quad . \qquad (5)$$

This hoped-for result, at once opened a field for investigation, in view of the importance which unimolecular reactions have assumed within recent years.

The foundations of chemical dynamics are, even now, on a rather arbitrary footing, and the examination of first-order changes such as this - of which few really good examples are known - is obviously the simplest point at which to attack the question. There is, however, another reason why we should look into this/

this reaction, for it is claimed by some chemists, that a reaction, in which only one species of molecule is concerned, is impossible (except in the case of a radio-active change). In other words, a process which obeys equation (5) is not necessarily unimolecular (Cf Lowry, Trans. Farad. Soc. XVII, (3), 596).

This belief rests, in the first place, on the phenomenon of catalysis, which occurs to a marked extent, even with many first order chemical changes. Several reactions have been shown to be prevented entirely, by the removal of a trace of a second substance - usually water. For this reason, the carbon monoxide reaction was examined as regards the effect of solvents, acids and bases, and finally water. As will be seen, later, the question was also investigated by changing the method of carrying out the reaction.

A second reason for examining this reaction is to be found in the Lewis-Perrin theory, (Ann. de Phys. 1919, II, 5 and J.C.S., 109, 796) that all chemical reactions are caused by radiation - a theory which, up to the present, has been directly tested in but a few cases. It is first necessary to know whether the velocity constant varies with temperature according to the Arrhenius law:

$$\frac{d}{dT} (\log K) = \frac{Q}{RT^2}$$

The experiments with the ethoxy compound showed that this was the case. Now Lewis and Perrin predicted,

that/

that it would be possible to calculate, in the case of unimolecular reactions, the frequency (ν) of the active light from the relation, $Q = Nh\nu$ (Planck)

where Q = the heat of activation obtained from Arrhenius' equation above,

N = Avogadro's number.

The truth of this hypothesis could be tested for the derivatives of oxalacetic ester in two ways:

(1) By illuminating them strongly with light of the wavelength, calculated from the heat of activation.

(2) By photographing their absorbtion spectra.

More recently, an explanation of the velocity of unimolecular reactions, which relies solely on collisions, to supply the necessary energy of activation has been elaborated by Christiansen & Kramers. (Zeit. f. Phys. Chem. 104, 457). According to them the "active molecules", postulated by Arrhenius to explain his equation, have acquired by collision sufficient energy to bring them to a certain high quantum state (similar to that assumed by Bohr in the region of atomic structure). If A = probability, that an active molecule will decompose during one second then, they deduce:

$$K = A \times e^{-\frac{Ea - En}{RT}} = Ae^{-Q/RT}$$

Where/

Where E_a = energy of a molecule in the active state &

E_n = energy " " " normal "

This is simply the Arrhenius formula integrated.

Thus there are two fundamental constants characteristic of a unimolecular reaction: Q , the energy of activation or "critical increment" and $^1/_A$, the average "life" of an active molecule. We should get some insight into the nature of a unimolecular change if we can establish any regularities in the variations of the values of A and Q , in different circumstances. The "kohlenoxydspaltung" provides us with a favourable opportunity for, by changing the group - R, we obtain molecules of differing "stability". It is true that Cain & Nicoll (J.C.S. 83, 470) have measured the temperature variation of the rates of decomposition, of a number of related diazo compounds; but their results are not of use for our purpose as the reaction is only apparently unimolecular - the solvent water acting stoichiometrically.

The latter part of this research, then, consists in measuring the temperature variation of the reaction constant, in different derivatives. The radical , R , was in turn $-OC_2H_5$, $-CH_3$, $-H$, $-CH_2 \cdot COOC_2H_5$ and $-C_6H_5$.

PREPARATIVE.

Ethoxy oxalacetic (diethyl) ester.

Et-OOC.CO.CH (OEt). COOEt

The method used for this substance was slightly different to that recommended by Wislicenus & Scheidt. (Ber. 24, 432) 1 molφ. of sodium was cut into thin slices and placed in 14 parts by weight, of absolute ether. Absolute alcohol was slowly added and, when the action had practically ceased, diethyl oxalate was run in to dissolve the layer of sodium ethylate. More alcohol was then run in, followed by more diethyl oxalate. In all, 1 mol. of alcohol and 1.2 mols. of diethyl oxalate (refractionated : B.P. 182°C.) were added.

To this solution 1 mol. of ethoxy-acetic (ethyl) ester was added and the yellowish brown solution was allowed to stand for several days. The ethoxyacetate was prepared by the action of sodium ethylate in absolute alcohol on ethyl chloracetate and boiled at 150°C. (Schreiner, Annalen, 197, 8).

The ether solution was now shaken with water and the aqueous layer, containing the sodium salt of ethoxy oxalacetic ester, separated. The calculated quantity of 4N sulphuric acid was added to the cooled solution/

solution, and the oil separated by repeated extraction with ether, as described by W. & S. (loc. cit.). The ester boiled at 134°-7°C. at 8 mm.

Several preparations were made by this method but these were never so pure as when "alcohol free" sodium ethylate was used. The sodium salt of this ester does not crystallise from alcohol, so that the only possible method of purification was by fractionating in <u>vacuo</u>. By doing so three or four times, a product was obtained which boiled at 133°C. at 8 mm., over a range of less than two degrees. During the repeated distillations of course, carbon monoxide was formed by overheating and the product therefore contained ethoxy malonic ester. That the impurity was about 10% of the whole, was shown by the yield of carbon monoxide on complete decomposition.

<u>α Oxal-propionic ester</u>.

EtOOC.CO. $CH(CH_3)$.COOEt

In this case the sodium ethylate was prepared (alcohol free) by passing a stream of dry hydrogen into a large r-b flask, containing its alcohol solution. The white solid formed was eventually heated on an oil bath, in the hydrogen stream to 200°, for five hours. The ethyl propionate was fractionated before use, until it boiled at 97.3 - 98.3°C. Otherwise the preparation/

preparation was carried out as described by Arnold (Ann. 246, 329). Two such preparations were made and in both cases the yield was of the order of eighty per. cent. and the product very pure.

Prep. I. B.P. 120-121°C. at 14 mm.

II. 114°C. at 10 mm.

Oxalacetic ester.

EtOOCCO.CH_2.COOEt. (See Wislicenus, Ann. 246, 315).

In view of the success of the above method of preparing the condensing agent, this way was repeated with subsequent preparations. In the case of oxalacetic ester, the condensation product soon solidified from the ether solution, as the sodium salt. After extraction, a nearly theoretical yield boiled steadily at 115°C. at 11 mm. This preparation was kept for two or three months before use, when it was redistilled. It now boiled at 111° - 113° at 9 mm. and left a light brown syrup in the distilling flask. This is always obtained when oxalacetic ester is distilled. (Ber. 27, 794). A similar substance was always obtained from the ethoxy compound and may account for the difficulty of obtaining the latter in a pure condition.

Oxal-succinic ester.

COOEt. CO. CH.(COOEt.) CH_2. COOEt.

The diethyl succinate boiled at 209°C. after fractionation. The condensation was carried out as before, but no attempt was made to prepare the potassium salt. (Ber. 22, 885.). At the pressure of the water pump, Wislicenus found that a temperature of 150 - 160°C was required to distil the product, and that decomposition was fairly rapid at this temperature. (As will be seen later, the velocity has actually been measured at 150°C.) A Gaede mercury-pump was therefore used to obtain the vacuum, and with its help, it was possible to distil the ester without any decomposition at 115°C. at 0.8 mm. The pressure was recorded on a McLeod gauge. A second preparation by the same method gave a product boiling steadily at 111° at 0.77 mm.

Phenyl oxalacetic ester.

COOEt. CO. CHφ.COOEt.

The boiling point of this substance, at the pressure of the water pump, lies so high that Wislicenus was unable to distil it undecomposed. (Ber. 27, 1092). It was hoped, by using a better vacuum to accomplish this, as with the last compound. Phenyl acetic acid (M.P. 73°C) was prepared from benzyl chloride, via the cyanide (B.P. 227 - 233°)/

- 233° and recrystallised from boiling water. The ethyl ester was prepared using hydrochloric acid gas, and boiled sharply at 223·5°C. The reactants were mixed in molecular proportions as usual, and, in a few hours, the sodium salt crystallised in a yellow mass. The phenyl oxalacetic ester was separated,and water and ether removed by means of the water pump. A portion was then distilled with great care in the Gaede pump vacuum. With a pressure of 0.5 mm. the ester slowly distilled but, at the temperature of bath required (145°C) the decomposition was very rapid,so that the distillate consisted largely of phenyl malonic ester.

A further attempt was made to distil the substance, this time with a "Hyvac" oil pump and charcoal cooled in liquid air-to reduce the vacuum. The pressure rose so quickly, however, that this was found to be impossible.

All these compounds, especially the ethoxy-, absorb moisture greedily from the atmosphere so that, where there was a possibility of a preparation's being affected on this account, it was redistilled before use. Drops of an ester,exposed on a glass surface to the air,soon show fine transparent crystals. These consist of hydrated oxalic acid. The preparations, generally, were nearly colourless but sometimes had a bright yellow colour, when freshly distilled. This faded/

faded somewhat on standing for a few hours, and still further, on admitting the moisture of the atmosphere.

PRELIMINARY EXPERIMENTS

on the measurement of velocity. To follow the process of decomposition we have to measure the volume of carbon monoxide, evolved at any instant. Now, when a gas is formed in a liquid, it is a common thing to find the gas becoming greatly supersaturated before it is liberated as bubbles. If, therefore, an accurate estimate of the extent of reaction is to be formed, we must assist the removal of carbon monoxide from the liquid, either by simple agitation or by using a stream of another gas. Both methods have actually been employed, in the work to be described, but only the second enables us to measure the true velocity. The best gas to use for this purpose is carbon dioxide, for, by passing the mixed gases into a Schiff nitrometer, containing caustic potash solution, one can measure immediately, the volume of carbon monoxide.

The ester (about 0.5 gm.) was placed in a tube of the shape shown in figure 1. This tube was immersed to a depth of about 3 inches, in an oil-bath of steady temperature. A stream of carbon dioxide, bubbling continuously through the ester in the direction DCA, removed the carbon monoxide as it was formed. The longer arm (AC) of the U was about/

DIAGRAM 2.

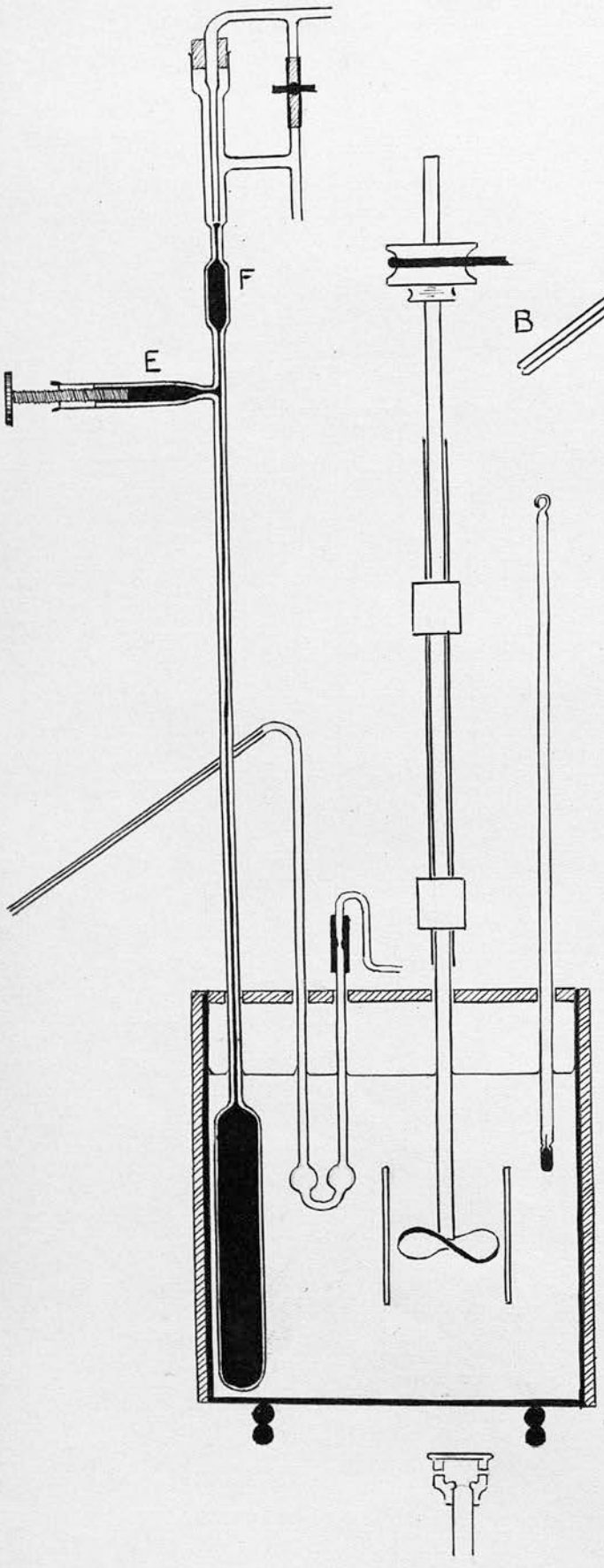
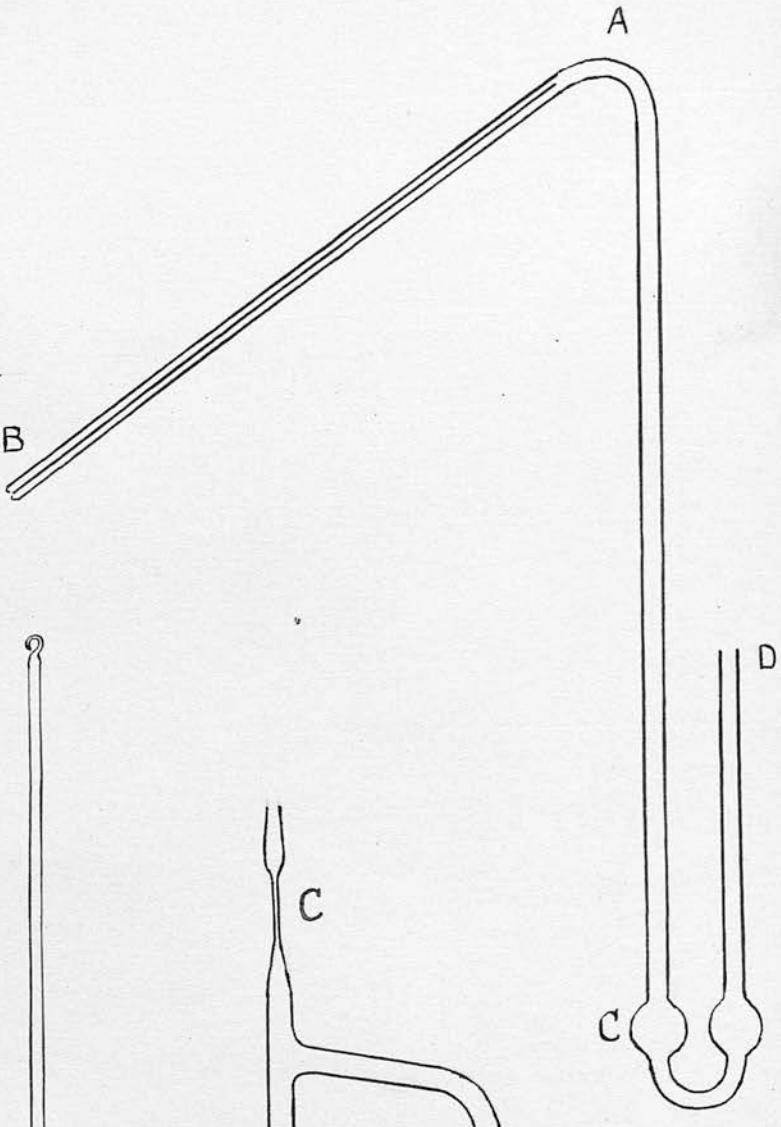


DIAGRAM 1.



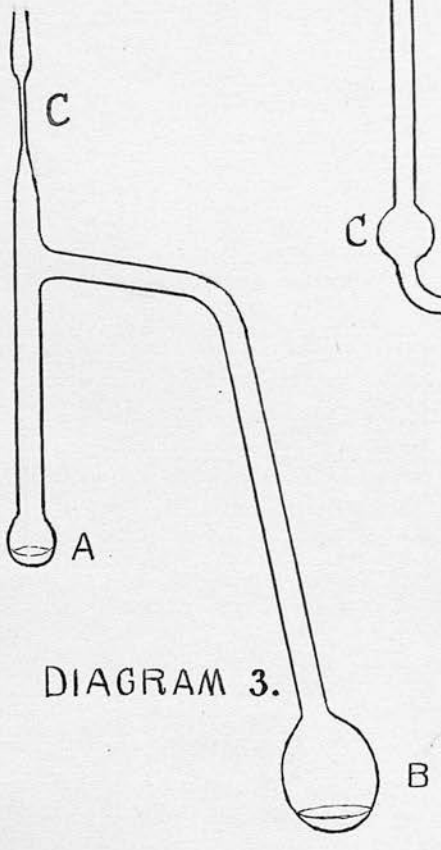


DIAGRAM 3.

about 6 inches long, was exposed to the air, and thus formed a condenser for the malonic ester, carried forward by the warm gases. The leading tube (AB) was made of fine capillary and was attached by pressure tubing, to the foot of the nitrometer. The carbon dioxide - in these experiments, from an ordinary Kipp's apparatus - was passed through three bubblers. The first contained a saturated solution of sodium bicarbonate and a little permanganate: the second and third contained concentrated sulphuric acid. The nitrometer was filled with a 1:1 solution of caustic potash stick.

Thermostat. At 180°C., where many of the experiments were done, the problem of keeping a steady temperature is not easy, so some time was devoted to this. The thermostat employed finally, was gas headed and the one used is shown in Fig. 2. Castor-oil was first used in the bath and, though there is no risk of its catching fire, it has the disadvantages of a bad odour and a tendency to thicken into a tar. Two paraffinoid oils, tried afterwards, showed the same weakness, and the oil had to be renewed when it showed signs of resinifying. The elevated temperature of the bath would not remain uniform throughout, unless the stirring were very violent. For this reason, as well as on account of the type of reaction-tube, there/

there was nothing to be gained by using a large bath. The stirrer was of the screw-type and turned so as to suck the oil upwards in a close-fitting brass cylinder, about 2 inches long. The power was supplied by an air-engine. The bath itself, was of enamelled iron and lagged with a thick sheet of asbestos, while the lid was made from asbestos board, stiffened with water-glass, and had openings for the thermoregulator, the stirrer, a thermometer and the reaction-tube.

The liquid in the thermoregulator was mercury on account of the temperature of working. This has the advantage of a high coefficient of expansion, good conductivity and high boiling-point but the disadvantage of its weight.

A diagram (2) of the thermoregulator is given. A large side arm (E) was provided with a screw, which adjusted the level of the mercury. With the aid of this, one could give the bath temperatures varying by 25°C., without removing or adding mercury. The bulb (F), above this, was provided, so that the liquid did not reach the side-tube on cooling down, and thus cause trouble when rewarmed, by the trapping of air. When the bath had been heated up for an hour or so the temperature kept very steady; occasional short fluctuations were never more than half a degree.

Method. The practical difficulty of measurement consists in striking a balance between two conflicting considerations. (1) The rate of the carbon/

carbon dioxide stream must not be so fast as to carry the vapour of either of the esters over the top of the condenser (past A). (2) The stream of gas must be made as rapid as possible, in order to ensure that, at any instant, the amount of carbon monoxide which has not reached the nitrometer is very small. This gas will be found dissolved in the esters and - mixed with carbon dioxide - in the space from the surface of the ester to the mercury of the nitrometer. To this end, the volume of the condenser and leading tube was designed to be as small as was consistent with efficient condensation.

It is obvious that the errors, due to these causes, will be less, the slower the rate, for, when the carbon monoxide is formed slowly, it is possible to sweep out of the system all but a negligible trace of the gas. Thus the measurements at lower temperatures may be regarded as more trustworthy. Again, the readings, in the later stages of any particular experiment, will be more correct than near the beginning.

It may be judged from the above, that one should not interrupt the stream of gas by levelling the liquid in the nitrometer, when taking a reading. There is another, even more cogent reason, for this - as will be seen later. Readings of the volume of carbon monoxide were therefore taken, with the reservoir of the nitrometer in a lowered and fixed position, such that/

that the gas stream continued. The true volume was obtained by applying a correction (C), from a previously constructed calibration curve. The accuracy of the calibrations was first tested, by weighing quantities of water run from the nitrometer - (as from a burette). The nitrometer was then charged with 50% caustic potash and the change in volume, on lowering the reservoir to the standard position, noted for various enclosed volumes of air. The results of this are given in table 1 (p. 15b) and the gross correction is plotted against the observation in Graph I, which was used in all experiments with this nitrometer.

The method of working was as follows: Enough ethoxy-ester, to give about 50 cc. of carbon monoxide, was run, by means of a long-pointed pipette, into the reaction-tube, which was then connected by thick rubber-tubing to the carbon dioxide supply and the nitrometer, respectively. A stream of carbon dioxide was passed for about an hour, to clean out the air from the system. Meanwhile the bath was adjusted to the desired temperature (183.5°C). After ~~filling~~ the nitrometer had been filled with fresh caustic potash solution, the reaction-tube was placed in the bath and the time noted. Readings of the time and uncorrected volume of carbon monoxide were then taken, at intervals of roughly three cc., until the bulk of the gas had come off. The stream of gas, which at first had been kept as/

GRAPH. 1.

CALIBRATION CURVE FOR NITROMETER.

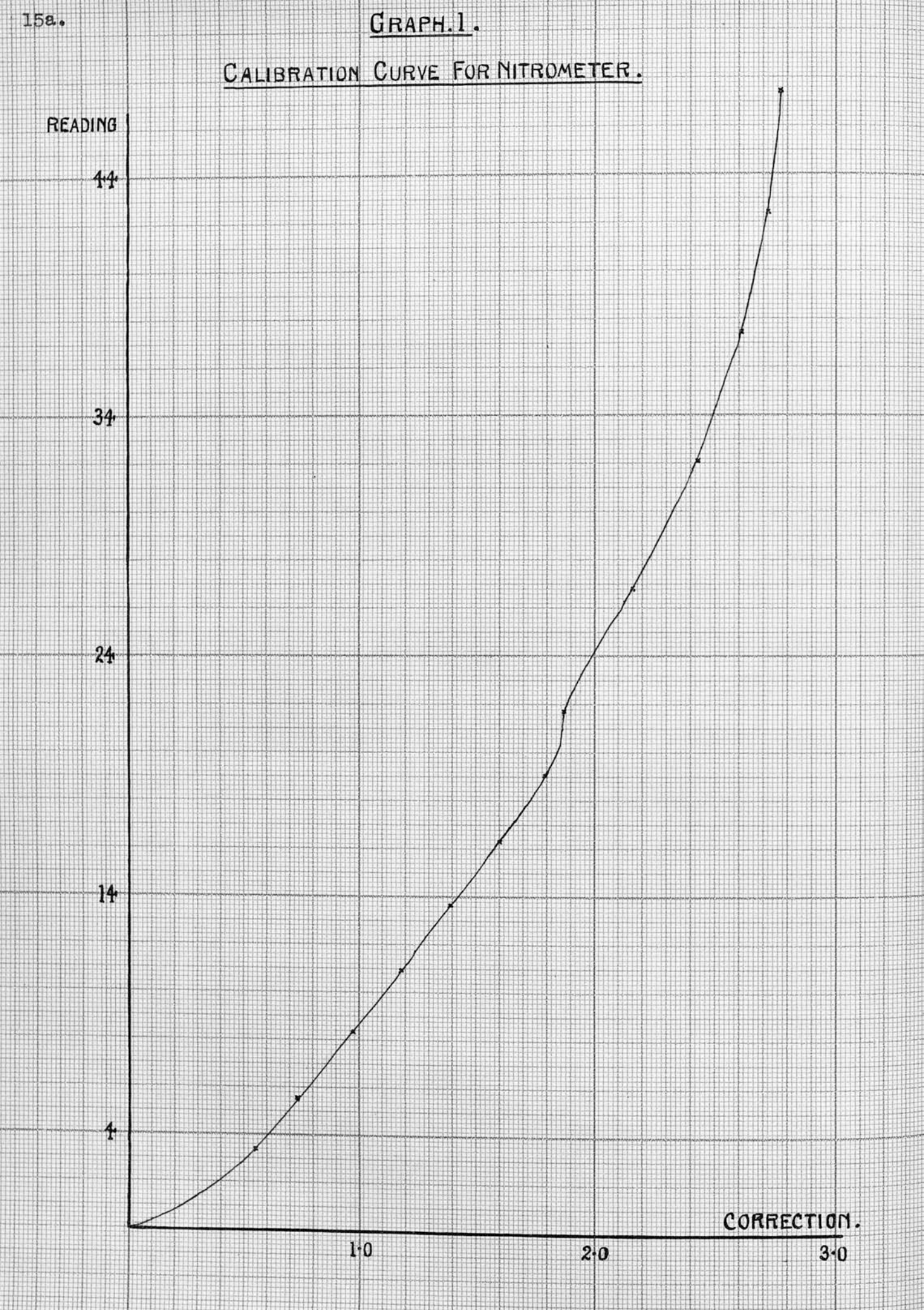


TABLE 1.

Calibration table for 100 cc. nitrometer.

Reading with reservoir lowered	Correction for reduc^{n}. of press	Error in Graduation	Gross Correction
3.40	0.33	0.22	0.55
5.55	.50	.23	.73
8.35	.75	.22	.97
10.95	.95	.23	1.18
13.65	1.15	.24	1.39
16.30	1.35	.25	1.60
19.05	1.55	.24	1.79
21.75	1.65	.22	1.87
26.80	1.95	.21	2.16
32.10	2.20	.23	2.43
37.45	2.40	.21	2.61
42.40	2.50	.22	2.72
47.45	2.55	.22	2.77
52.60	2.60	.17	2.77
57.50	2.60	.18	2.78
62.45	2.50	.13	2.63

as fast as was possible,(without causing distillation) was now made slower. The value of the final volume was read when no further increases took place. All gas volumes were measured at, or converted to, the temperature and pressure prevailing during the early part of the experiment. Generally, the final volume only, had to be corrected for this purpose.

In the expression for the unimolecular constant, $k = \frac{1}{t} \log_{10} {}^{a}/_{a-x}$, $\underline{a}$ is the total number of reacting molecules at the start, and $\underline{x}$ the number which have reacted after time $\underline{t}$. Both of these were measured by the corresponding volumes of gas and as they occur in the expression only as ${}^{a}/_{a-x}$, the <u>ratio</u> of two gas volumes, there was no necessity to convert to standard temperature and pressure, for comparison with other constants.

A graphical method was employed to find at what instant the reaction could be regarded as starting: the values of $\log {}^{a}/_{a-x}$ were first calculated. These were then plotted against the observed times . (t_1 in table). If the decomposition is unimolecular, the points should lie on a straight line - as was in general the case. By producing this line to cut, $\log {}^{a}/_{a-x} = 0$, the required value of $t(t_0)$ was obtained.

A series of results of a typical early experiment is appended, together with this graph. (Table 2,GraphII.)

The/

GRAPH 2.

EXPT. XXVII: ETHOXY-OXALACETIC ESTER AT 183·5°C.

SEE TABLE 2.

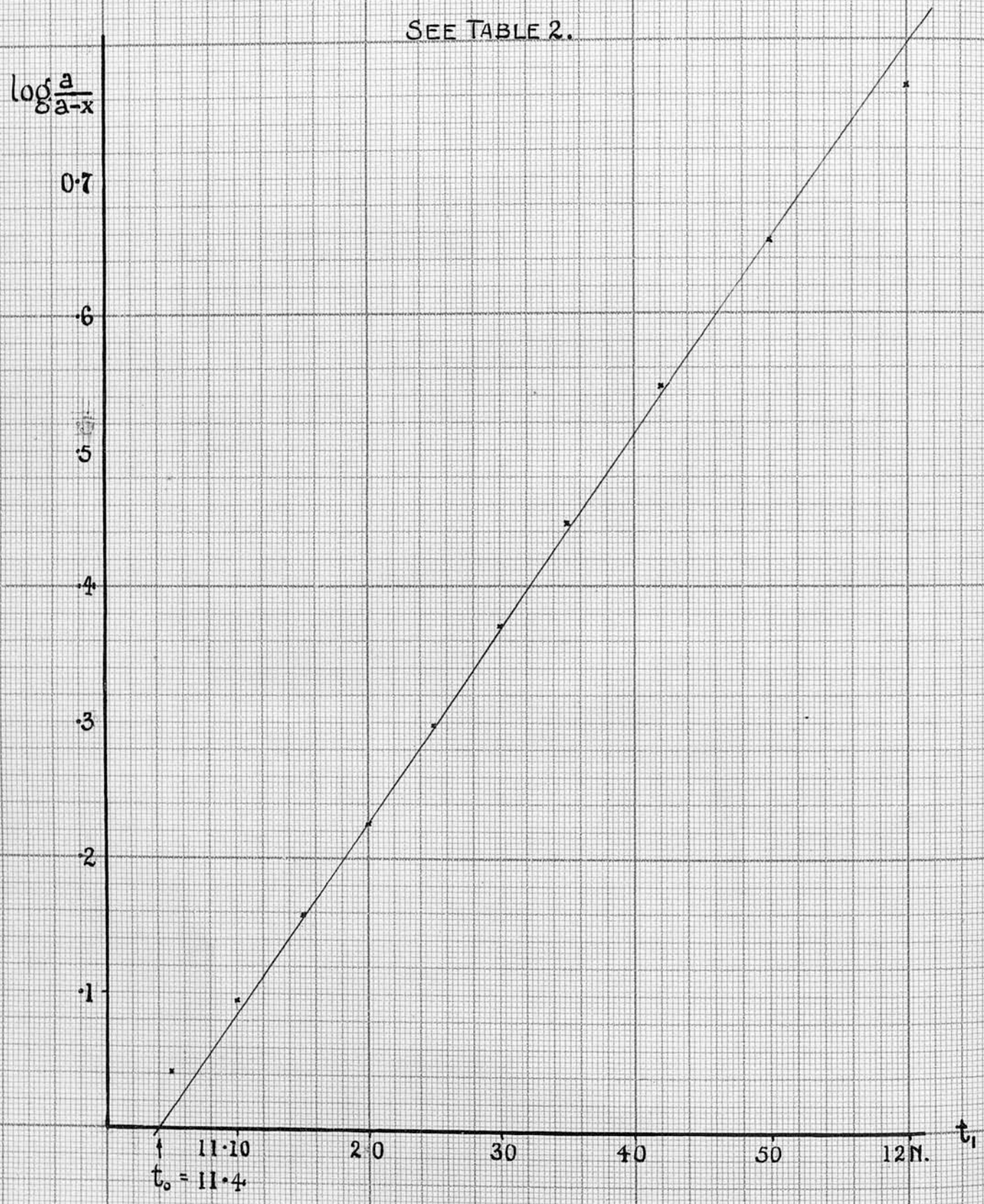


TABLE 2.

Ethoxy oxalacetic ester at 183.5°C.

$a = 40.0 + 5.8 = 45.8$; $\log a = 1.6609$; $t_0 = 11.4$.

t_1	v	* c	x	45.8-x	$\log_{10} a/a-x$	t	K x 10^4
						(min)	
10.59	start						
11.2	1.9	.15 + .2	1.45	44.35	.0140		
11.5	4.6	.3 "	4.1	41.7	.0408	1	(408)
11.10	10.0	.8 "	9.0	36.8	.0951	6	(158)
11.15	15.4	1.2 "	14.0	31.8	.1585	11	144.
11.20	20.2	1.45 "	18.55	27.25	.225	16	141
11.25	24.6	1.65 "	22.75	23.05	.298	21	142
11.30	28.3	1.8 "	26.3	19.5	.371	26	142.5
11.35	31.5	1.9 "	29.4	16.4	.446	31	144.
11.42	35.0	2.0 "	32.8	13.0	.547	38	144
11.50	37.9	2.05 "	35.65	10.15	.654	46	140
12 noon	40.25	2.1 "	37.95	7.85	.766	56	137
12.16	42.3	2.1 + .2	40.0	5.8	.897	72	(124)
Change to 2nd nitrometer							
1.1	1.92						
∞	5.7	+ .1	5.8				

* Not from table 1.

Average : $k = \underline{\underline{141.8 \times 10^{-4}}}$

The decomposition is that of ethoxy oxalacetic ester at 183.5°C. The first two columns show the observed times (t_1) and volumes (v). c is the total volume correction obtained from a table similar to Table 1. The fourth column, x, is the corrected volume, i.e. (v - c), while the next two give the values of (a - x) and $\log a/a-x$. "t" is simply the observed time, t_1, minus t_o - the calculated zero time. The values of k are in (min.$^{-1}$ x $\log_{10}$).

In this experiment, as in several others, a second nitrometer (connected to the leading tube by means of a Y - join) was used for the later stages of the experiment. The object was to obviate any error introduced by the caustic potash in the first, becoming saturated with Carbon dioxide.

It will be seen at once from the graph, that the reaction is unquestionably unimolecular and this is borne out by the values of k in the table. The constancy of k remains good through about two-thirds of the experiment, - and the deviations at the start and finish, may therefore be attributed to secondary effects or to the experimental method. At the beginning, 15 minutes are required before the disturbance is eliminated. As regards the fall of the constant at the end, experiments with the methyl derivate will be quoted, in which this is absent, and so the effect is possibly associated with a side reaction peculiar to the ethoxy compound.

ALTERATIONS IN METHOD.

The early experiments are too numerous to quote in full, and in the main, only the results will be given. In the course of them, many ~~different methods~~ variations were tried in the method of measurement and of calculating the result. Of course, the first aim was to see how accurately it was possible to repeat a result. At the same time, the second question - mentioned in the introduction - was attacked, namely, whether one could influence the reaction (kinetically) by the addition of other substances.

The main difficulty throughout was the choice of the best method for determining **a** - the total volume of gas evolved. In the first place, it could not be obtained by calculation from the weight of substance used, as the ethoxy compound could not be prepared pure enough to give the theoretical yield, according to equation (3). It is possible that this loss of carbon monoxide was due to the side-reaction, noticed by Wislicenus in the case of the parent compound - exalacetic ester. He heated this substance quickly and identified in the distillate, pyruvic ester, carbon dioxide and alcohol. These would be formed, by adding a molecule of water to oxalacetic ester itself:

$$COOEt.CO.CH_2.COOEt + H.OH = COOEt.CO.CH_3 + CO_2 + HOEt.$$

The water is presumably obtained by the condensation of other molecules of oxalacetic ester, to form the viscous oil, which remains in the distilling flask. Such an oil was always found when the ethoxy compound was distilled.

In the second place, it was not always easy to say exactly when the reaction had stopped, and hence to use the final volume as the measure of "a". In most experiments with the ethoxy derivative, the reaction seemed to persist at the end for longer than it ought - as judged by a simple calculation based on the first order law. This phenomenon was probably connected with the side-reaction mentioned above.

The third difficulty was the presence of air in the carbon dioxide from a Kipp's apparatus. In very early experiments this was ignored but later, steps were taken to eliminate or correct for it.

Value of "a"

1. Instead of considering the reaction represented by the total volume of gas, one may consider only a portion of the experiment, from say, 20 minutes after the introduction of the tube into the bath.
2. The reaction may be hastened, at the end, by raising the temperature of the bath.

3. In a number of experiments, the volume of nitrogen in the collected gas was measured by Hempel's method, and deducted from the value of "a". In such cases corrections were also applied to the value of "x". The amount of oxygen was small.

Value of "x".

As already mentioned, the values of "x" were always corrected for the errors of the graduation and for the lowering of the nitrometer reservoir. As regards the correction for air present, this was done in either of two ways: (1) On the basis of a blank experiment with the "Kipp" to be used. (2) On the assumption that the nitrogen measured, as above, came over at a constant rate.

There is, however, good reason to suppose that less error is introduced, by not correcting for any air in "a" or "x", than by assuming that equal volumes of air reach the nitrometer, in equal times. As an experiment proceeded, the amount of carbon monoxide to be swept out, diminished and therefore, the stream of carbon dioxide was steadily reduced. Thus, the volumes of air brought over would diminish exponentially at very much the same rate, as the volumes of carbon monoxide. Hence, though there may be a considerable amount (2%) of air in the gas collected, with the experiments of this group, no corrections have been made in the tables.

Value of t_o

One point is to be noted with regard to the graphical method of determining the zero time. As has been seen on the graph of the experiment already quoted, there is a displacement of the points on the curve, during the first fifteen minutes. This may produce a portion of the curve, which approximates to a straight line, but does not represent the true velocity. Overlapping this effect is a weakness, inherent in the stream method employed, that it is unable to show the fast rate of decomposition to be expected at the start - especially in experiments at higher temperatures. Fortunately, this trouble exists in only a few experiments, for the graph generally leads to a very definite value of t_o.

By the methods, outlined above, it was easy on repeating a determination to obtain a value differing by not more than 5% from the first - provided the details of the experiment were kept the same. For example, the experiment XL was carried out under exactly the same conditions as experiment XXVIII , (Table 2) already quoted. See table 3, p. 27.
Ethoxy derivative at 183.5°C: Average $k = \underline{142.9 \times 10^{-4}}$

The agreement of this value with that already given (141.8) is very satisfactory and is not exceptional. However, other early experiments done with the/

the ethoxy compound,do not show such good agreement. In these the method of working was not just the same. It appears from later experiments, that the probable cause of differences bigger than 5% is lack of care with the carbon dioxide stream. If this is too fast, gradual distillation of the undecomposed substance will lead to an apparently bigger velocity constant.

INFLUENCE OF SOLVENTS, ACIDS AND BASES.

In testing for the presence of solvent catalysis, the choice of solvents is not large,as the substance must have a small vapour pressure at 180°C. The object was to use a solvent,which would not act chemically on the ester. Brom-naphthalene seemed to be suitable. (B.P. 277°C) It was mixed with an equal quantity of the ethoxy compound and the mixture decomposed in the same type of reaction-tube as before. The results are shown in table 4, p.28.

Experiment XXIX: Average $k = 153.1 \times 10^{-4}$

An earlier experiment with brom-naphthalene gave 158 while,with the isomeric α and β methyl-naphthyl ethers the results were 158 and 153 respectively. (see summary, Table 9, p. 33 .) The average of these values is about ten per cent higher than the velocity in the case of the pure substance. The effect, however, is small enough to justify our supposing that inert/

inert solvents of this kind exert little catalytic influence on the velocity. The small increase, observed, is probably due to some secondary effect connected with the escape of carbon monoxide from the liquid.

The next question was ionic catalysis. For this purpose, admixtures of 5 - 10% of the weak acids, benzoic and salicylic, were tried, without result. Concentrated sulphuric acid was not feasible as, at 180°C, charring would inevitably occur. The alternative was gaseous hydrochloric acid, but, since this would soon have been swept away by the carbon dioxide, it was thought that a stream of hydrochloric acid gas might be used instead of the latter. Crystallisation of potassium chloride in the nitrometer soon made this impossible. The catalyst was therefore introduced into the carbon dioxide by a Y-join and in a proportion of about one-fourth. Under these conditions, the chloride remained in solution. The results are given in table 5, p. 29.

Experiment XXXIX : Average $k = \underline{143.3 \times 10^{-4}}$

It seems, from this result, that addition of $H^{\cdot}$ leaves the velocity unaltered. It might be argued that the carbon dioxide of the stream is itself acting as a catalyst and means were, therefore, sought whereby the reaction could be carried out in its absence. /

absence. This was achieved by using a stream of sulphur dioxide. On a first trial potassium sulphite was found to crystallise out very easily from the alkali, but this difficulty was overcome by using, for absorption, a solution of potash containing a fair amount of carbonate. The result was as follows at 183.5°.

Experiment XXXVIII : Average k = $\underline{128 \times 10^{-4}}$

That this is not definite evidence for catalysis, is shown by the summary (Table 9). The early experiments with the ethoxy derivative gave two sets of results at 183.5°C. One set lay near 125 and the second lay near 140. It is thus probable that the velocity using sulphur dioxide, is the same as when using carbon dioxide.

After examining the influence of these acidic bodies, I decided to ascertain whether bases would have any more effect. An early experiment, using quinoline in the ratio, 1 of quinoline to 5 of ester, gave the velocity at 183.5° as $\underline{125 \times 10^{-4}}$.
It was noticed, at the conclusion of this experiment, that the ester was badly charred. Later, caustic potash in powder form was added to the ester and the velocity of decomposition determined. The results are given in table 6, p. 30 .

Experiment XXXV : Average k = $\underline{87.8 \times 10^{-4}}$

Here,/

Here, then, the velocity was markedly slower but, again, the residue in the reaction tube was badly charred. In addition, the constant does not persist for so long as in the average experiment, so that a side-reaction is probably taking place.

Finally, there is the question of whether moisture plays any part in the reaction. In experiment XXXII water was mixed with the ester to the extent of 25 per cent., by weight, at the start of the experiment. The results in table 7, show that, under these circumstances, at least, water is without effect on the velocity. Thus any moisture which reaches the ester, while the latter is being placed in the reaction-tube, can be ignored. The high temperature and the use of thoroughly dry carbon dioxide, rendered it likely that the water had been driven off from the ester very soon. In the next experiment, then, the sulphuric acid bubblers were omitted and the carbon dioxide was therefore saturated with moisture. At the same temperature as before, the constant was found to be 89×10^{-4} and held good for about half the experiment. As with caustic potash, the residue was very much charred and in view of the extent of this side-reaction, it is doubtful if any legitimate conclusion can be drawn as to the apparent retardation.

The problem of the rôle (if any) of water, in the/

the reaction, was approached from another point of view, by drying the ethoxy ester, very thoroughly, for some weeks, over phosphorus pentoxide. It was then carefully transferred to the reaction-tube and the velocity of decomposition measured as usual. The experimental results appear in table 8, p. 32 .

Experiment XXXIV : Average k = $\underline{121.4 \times 10^{-4}}$

This result, along with that of experiment XXXII show that, if moisture is necessary for dissociation (as Baker's experiments would lead us to suppose) then it is formed in sufficient quantity, by a side-reaction, while the decomposition proceeds.

In the experiments, whose results are given in tables 3 to 8, the method was the same throughout. Two nitrometers were always used. As no special precautions were taken to remove air from the carbon dioxide, the gas collected in the nitrometer generally contained about 1-2 cc. of this impurity. The yield of carbon monoxide was, in most experiments, about 80 - 90% of the theoretical.

Other experiments were made on the subject of the presence of catalysis and the results of these have been summarised in table 9. It will be noticed that, despite the discrepancies through the group as a whole, there is a tendency for experiments performed together, to give comparable results. The average value of the constant at 183.5°C. omitting experiments 35 and 36 is 138.9×10^{-4}.

Experiments with ethoxy-oxalacetic ester at 183.5°C.
(Tables 3 to 8)

TABLE 3.

Expt. XL : "Ethoxy" at 183.5°C.

a = 49.6 cc ; log a = 1.6955 ; t_o = 11 h. 0.8 m.

t_1	v	c *	x	49.6-x	log a/a-x	t	K x 10^4
10h 58m	start	-	-	-	-	-	-
11.2	3.6	0.55	3.05	46.55	.0275	1.2	(229)
.6	9.0	1.0	8.0	41.6	.0764	5.2	(147)
.9	12.9	1.35	11.55	38.05	.1151	8.2	140.2
.12	16.6	1.6	15.0	34.6	.1564	11.2	140.0
.15	20.1	1.85	18.25	31.35	.199	14.2	140.5
.18	23.4	1.95	21.45	28.15	.246	17.2	143.0
.21	26.3	2.15	24.15	25.45	.290	20.2	143.5
.25	29.7	2.3	27.4	22.2	.349	24.2	144.5
.30	33.4	2.5	30.9	18.7	.424	29.2	145.0
.35	36.4	2.6	33.8	15.8	.497	34.2	145.5
.40	38.8	2.65	36.15	13.45	.567	39.2	144.5
.45	40.8	2.7	38.1	11.5	.635	44.2	143.5
.53	43.3	2.7	40.6	9.0	.741	52.2	142.0
12.1	44.9	2.75	42.15	7.45	.823	60.2	(137)
.12	46.4	2.75	43.65	5.95	.921	71.2	(130)
1.11	48.3	2.8	45.5				
Second nitrom^r ∞	+ 4.1		49.6				

Average : $k = 142.9 \times 10^{-4}$

* Corrections not made from table 1 (see also table 4.)

TABLE 4.

Expt. XXIX : "Ethoxy" in brom-naphthalene.

$a = 22.8$; $\log a = 1.3579$; t_o = 11 h. 0 m.

t_1	v	c*	x	22.8-x	$\log {}^{a}/_{a-x}$	t	K x 10^4
10.55	start	-	-	-	-	-	-
11.3	3.1	0.2	2.9	19.9	.0587	3	(196)
.6	5.0	.35	4.65	18.15	.0990	6	(165)
.10	7.3	.55	6.75	16.05	.1525	10	152.5
.15	10.0	.75	9.25	13.55	.226	15	150.5
.20	12.45	.95	11.5	11.3	.305	20	152.5
.25	14.5	1.1	13.4	9.4	.385	25	154
.31	16.55	1.25	15.3	7.5	.483	31	156
.40	18.8	1.35	17.45	5.35	.630	40	157.5
.52	20.7	1.45	19.25	3.55	.808	52	155
12.8	22.0	1.5	20.5	2.3	.996	88	147
1.11	23.4	1.6	21.8	1.0	1.358	131	(104)
Second nitrom^r. ∞	+ 1.0		22.8				

Average : $k = 153.1 \times 10^{-4}$

TABLE 5.

Expt. XXXIX : "Ethoxy", with HCl in CO_2.

a = 44.65 + 3.95 = 48.6 cc ; $\log a$ = 1.6866 ; t_o = 11 h.36.3 m.

t_1	v	c	x	48.6-x	$\log a/a-x$	t	K x 10^4
11h 34m	start	-	-	-	-	-	-
.41	8.6	1.0	7.6	41.0	0.0738	4.7	(157)
.44	12.5	1.3	11.2	37.4	.1137	7.7	(147.5)
.47	16.0	1.55	14.45	34.15	.1532	10.7	143.
.50	19.4	1.8	17.6	31.0	.1952	13.7	142.5
.53	22.4	1.9	20.5	28.1	.238	16.7	142.5
.56	25.3	2.1	23.2	25.4	.282	19.7	143.
12. 0	28.7	2.25	26.45	22.15	.341	23.7	143.5
.6	33.0	2.3	30.7	17.9	.434	29.7	146.
.10	35.3	2.55	32.75	15.85	.486	33.7	144.
.15	37.7	2.6	35.1	13.5	.556	38.7	143.5
.20	39.65	2.65	37.0	11.6	.622	43.7	142.
.30	42.4	2.7	39.7	8.9	.737	53.7	(137)
.40	44.25	2.75	41.5	7.1	.835	63.7	(131)
1.30	47.4	2.75	44.65	3.95	1.090	113.7	
Second nitrom^r. ∞	+3.95		48.6				

Average : $\underline{\underline{k = 143.3 \times 10^{-4}}}$

TABLE 6.

Expt. XXXV : "Ethoxy", with KOH added.

a = 21.25 + 3.95 = 25.2 cc ; log a = 1.4014 ; t_o = 12 h 0.5 m.

t_1	v	c	x	25.2-x	log $^{a}/_{a-x}$	t	K x 10^4
12.3	start	-	-	-	-	-	-
.9	4.7	0.65	4.05	21.15	0.0761	8.5	89.6
.13	6.55	.8	5.75	19.45	.1125	12.5	90.0
.17	8.3	.95	7.35	17.85	.1498	16.5	91.0
.20	9.45	1.05	8.40	16.8	.1761	19.5	90.4
.26	11.5	1.2	10.3	14.9	.228	25.5	89.5
.33	13.4	1.4	12.0	13.2	.281	32.5	86.4
.38	14.55	1.45	13.1	12.1	.319	37.5	85.1
.47	16.15	1.6	14.55	10.65	.374	46.5	80.5
1.5	17.95	1.7	16.25	8.95	.450	64.5	(70)
.27	19.2	1.8	17.4	7.8	.509	86.5	(59)
3.16	23.25	2.0	21.25				
Second nitrom^r ∞	+ 3.95		25.20				

Average : $\underline{\underline{k = 87.8 \times 10^{-4}}}$

TABLE 7.

Expt. XXXII : "Ethoxy", with water added.

$a = 32.9 + 1.7 = 34.6$; $\log a = 1.5391$; $t_o = 12$ h. 7 m.

t_1	v	c	x	34.6-x	$\log {}^{a}/_{a-x}$	t	K x 10^4
12.3	start	-	-	-	-	-	-
.9	3.2	0.5	2.7	31.9	0.0353	2	(176.5)
.12	5.4	.7	4.7	29.9	.0634	5	126.8
.15	7.9	.9	7.0	27.6	.0982	8	122.8
.20	11.85	1.25	10.6	24.0	.1589	13	122.3
.25	15.4	1.5	13.9	20.7	.223	18	124.0
.30	18.45	1.75	16.7	17.9	.286	23	124.4
.35	21.0	1.85	19.15	15.45	.350	28	125.0
.40	23.2	1.95	21.25	13.35	.414	33	125.5
.59	28.9	2.3	26.6	8.0	.636	52	122.3
1.15	31.3	2.4	28.9	5.7	.783	68	(115)
2.20	34.35	2.5	31.85	2.75	1.100	133	(83)
4.32	35.40	2.5	32.9				
Second nitrom^r ∞	+ 1.7		34·6				

Average : $k = 124.1 \times 10^{-4}$

TABLE 8.

Expt. XXXIV : "Ethoxy": previously dried over P_2O_5.

a = 23.9 + 1.8 = 25.7 cc ; log a = 1.4099 ; t_o = 11 h. 20 m.

t_1	v	c	x	25.7-x	log $^a/_{a-x}$	t	K x 10^4
11.17	start	-	-	-	-	-	-
.23	2.8	0.5	2.3	23.4	0.0407	3	(136)
.26	4.65	0.65	4.0	21.7	.0734	6	122.3
.30	7.05	0.85	6.2	19.5	.1199	10	119.9
.36	10.4	1.1	9.3	16.4	.195	16	121.9
.40	12.35	1.3	11.05	14.65	.244	20	122.0
.45	14.45	1.45	13.0	12.7	.306	25	122.4
.50	16.25	1.6	14.65	11.05	.367	30	122.3
12 noon	18.85	1.75	17.1	8.6	.475	40	118.8
.12	20.85	1.85	19.0	6.7	.584	52	(112)
3.32	26.0	2.1	23.9	1.8	1.155	252	
Second nitrom^r. ∞	+ 1.8						

Average : $k = 121.4 \times 10^{-4}$

TABLE 9.

Summary of First Experiments with Ethoxy-oxalacetic Ester.

Experiment	Solvent or Catalyst.	Proportion.	K x 10^{-4}
	At 184°C.		
X	Benzoic acid.	$\frac{1}{10}$ mol.	124
XIV	Quinoline. *	$\frac{1}{5}$ mol.	125
XV	-	-	127
XXII	β Naphthyl-methyl ether.	3 : 2	153
XXIII	α " " "	1 : 1	158
	At 183.5°C.		
XXIV	Brom-naphthalene.	1 : 1	158
XXV	-	-	143
XXVII	-	-	141
XXVIII	-	-	141.8
XXIX	Brom-naphthalene.	1 : 1.2	153.1
XXXII	Water.	1 : 4	124.1
XXXIV	Ester dried over P_2O_5.	-	121.4
XXXVI	Moist CO_2 stream. *	-	(89)
XXXV	Powdered KOH. *	$\frac{1}{5}$ mol.	(87.8)
XXXVIII	Sulphur dioxide stream.	-	128
XXXIX	HCl in CO_2 stream.	-	143.3
XL	-	-	142.9

Average velocity (omit 35 & 36) = 138.9×10^{-4}

* Charring.

THE "SLOW" REACTION.

(Intermittent stream of carbon dioxide)

We can infer from these results, that there is no evidence for a positive catalytic influence in this reaction, for, in no case, has the velocity been markedly increased. Where it is decidedly less we find the primary reaction accompanied by a profound side-reaction. It has, however, been possible to show the phenomenon of 'anticatalysis'.

The discovery was made when I was trying to reduce the amount of air, introduced into the collected gas. This problem was attacked by using a special type of Kipp's apparatus - to be described later - and also by reducing the amount of carbon dioxide used. It was supposed, that, by reducing the number of readings and by using the stream of carbon dioxide for only a short time, (2 minutes in fact) before each reading, that the velocity measured should be the same. However table 10, p.38, shows the type of result that was obtained in this way, again using the ethoxy compound at 183.5°C.

Experiment LXV : Average $k = \underline{89 \times 10^{-4}}$

At first, the low value was attributed to impurity in the substance but when the ester was redistilled the velocity remained unchanged. It was then/

then noticed that the reaction-tube used in LXV had thicker walls than previously, which suggested that faulty heat conduction might be responsible for the discrepancy. A reaction-tube with two platinum wire infusions was then employed but with same result. However, when a continuous stream of carbon dioxide was tried once more, it became evident that this was at the root of matter for the value $\underline{\underline{138.2 \times 10^{-4}}}$ as in table 9, was again obtained. The following are the results of five experiments using the method of LXV :- LX; 82.0×10^{-4}, LXI; 94.8, LXV; 89.0, LXVII; 85.4, LXVIII; 95.4.

Average $\underline{89.4 \times 10^{-4}}$

In these experiments, the original object was in part attained, for the volume of nitrogen, measured at the conclusion, was generally about 0.5 cc.

The exact nature of this phenomenon is not at once evident. In the first place, it should be pointed out, that the retardation in velocity is real and not simply apparent; for it might be supposed, that in two minutes, all the carbon monoxide which had collected in the solution, would not be completely swept out. Thus the measurements would lag behind the real state of the reaction. Now, this was not the case, for it was obvious, in making the readings, that the accumulated carbon monoxide was driven from the liquid in about 30 seconds. There are three possible "explanations":/

"explanations": (1) It is conceivable that the agitation of the esters by the stream of gas, helps the reaction by providing a big effective surface. (2) The change may be reversible. (3) The carbon monoxide may act as an "anticatalyst" towards the reaction.

The improbability of reversibility in this reaction, was shown as follows: Some pure methyl malonic ester (B.P. 193°C.) was placed in the bulb A of a tube, shaped as in diagram 3, pg11a. The bulb B contained about ½ gm. of a mixture of 2 parts of concentrated sulphuric acid with 1 of formic acid. The whole was evacuated, with a Gaede pump, and sealed off at C. The formic acid mixture was then warmed with a bunsen flame, till no more gas was evolved. After bulb A had been heated for several hours in a bath at 170°C., the apparatus was left at room temperature for a fortnight. The tube was opened, the ester dissolved in alcohol and treated with ferric chloride. There was no trace of the wine-red colour, characteristic of methyl oxalacetic ester.

The question of hypotheses (1) and (3) will be dealt with later. Meanwhile, before leaving this "slow" reaction, it should be mentioned that an experiment with the same method was carried out with the ethoxy compound, at 173°C; here k was 20.9×10^{-4}. This means, in the Arrhenius formula, a temperature coefficient/

coefficient of 55,600 cals. which is exceptionally large.

Further, the decomposition of oxal-propionic ester was investigated, by the same means, with the result shown in Graph III, (Expt. LXXXVI) pg 38a. Here the values of log $^{a}/_{a-x}$ increase rapidly with regard to t. This means that the rate of reaction, as measured by the unimolecular constant, is getting faster and faster as the experiment proceeds. This is what we should expect, if the carbon monoxide acts as an anticatalyst.

In table 11, p. 39, the results of this experiment are given, the readings being taken with the KOH solution levelled, as in table 10. In the last column, the values of $^{x}/_{t}$ have been calculated and appear practically constant. This means that for almost the whole experiment, carbon monoxide is liberated at a constant speed. The significance of this result will be discussed later.

(Tables 10 and 11.)

TABLE 10.

Expt. LXV : "Ethoxy" at 183.5°C, with intermittent Stream of CO_2 (2 minutes before each reading.)

a = 44.3 ; log a = 1.6464 ; t_o = 2 h. 14 m.

t_1	v *	x=(v-0.2)	44.3 - x	log $^{a}/_{a-x}$	t	K x 10^4
2.2	start	-	-	-	-	-
.15	3.5	3.3	41.0	0.0336	1	(336)
.28	11.1	10.9	33.4	.1227	14	87.8
.44	19.4	19.2	25.1	.247	30	82.2
3.11	30.5	30.3	14.0	.500	57	87.9
.39	38.0	37.8	6.5	.833	85	98.0
∞	44.5	44.3				

Average : $k = 89.0 \times 10^{-4}$

(* The liquid in the nitrometer was levelled, before taking these readings, and v has therefore to be corrected only for the error in the graduation.)

GRAPH II.

EXPT. LXXXVI: OXALPROPIONIC ESTER (INTERMITTENT CO_2)

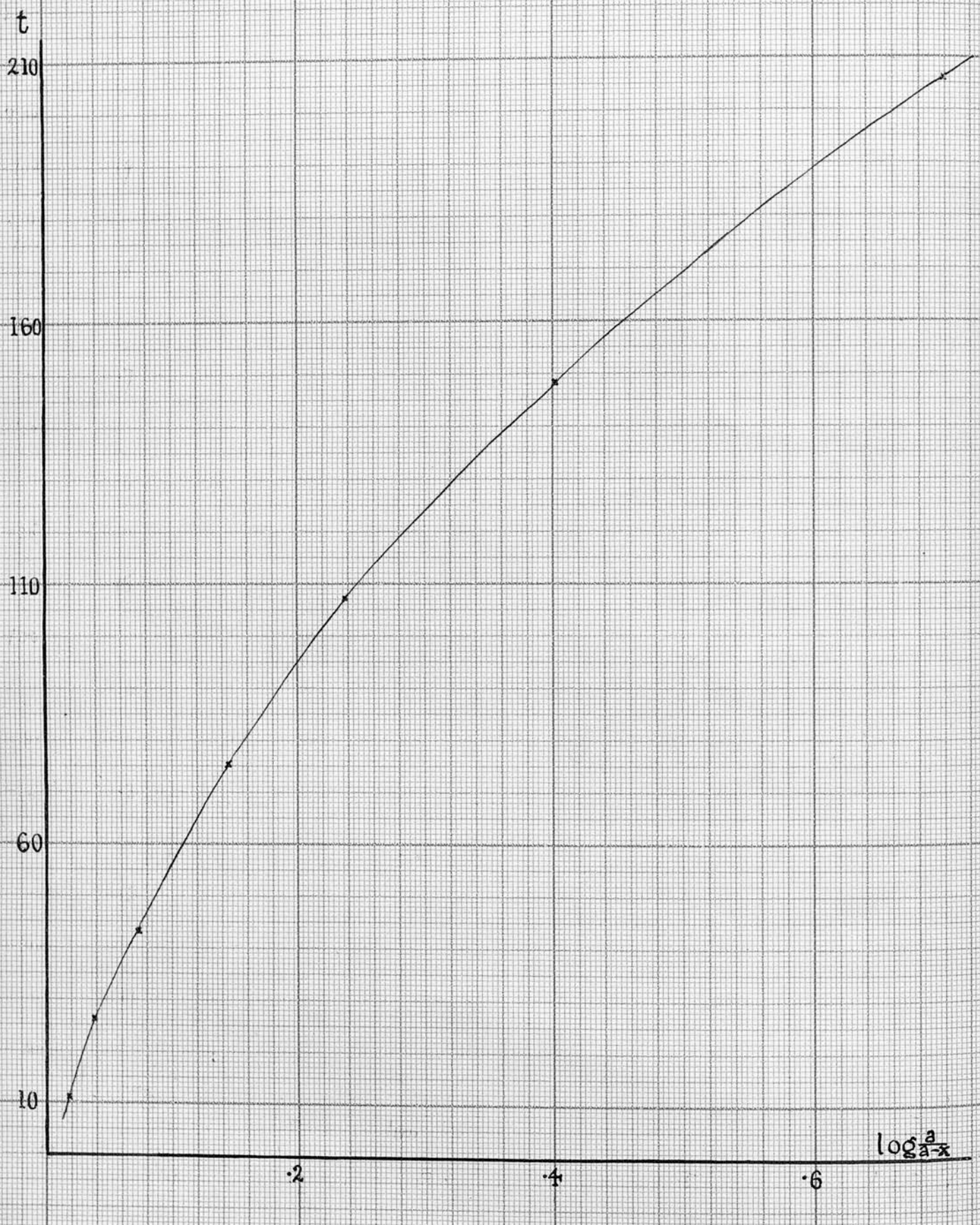


TABLE 11.

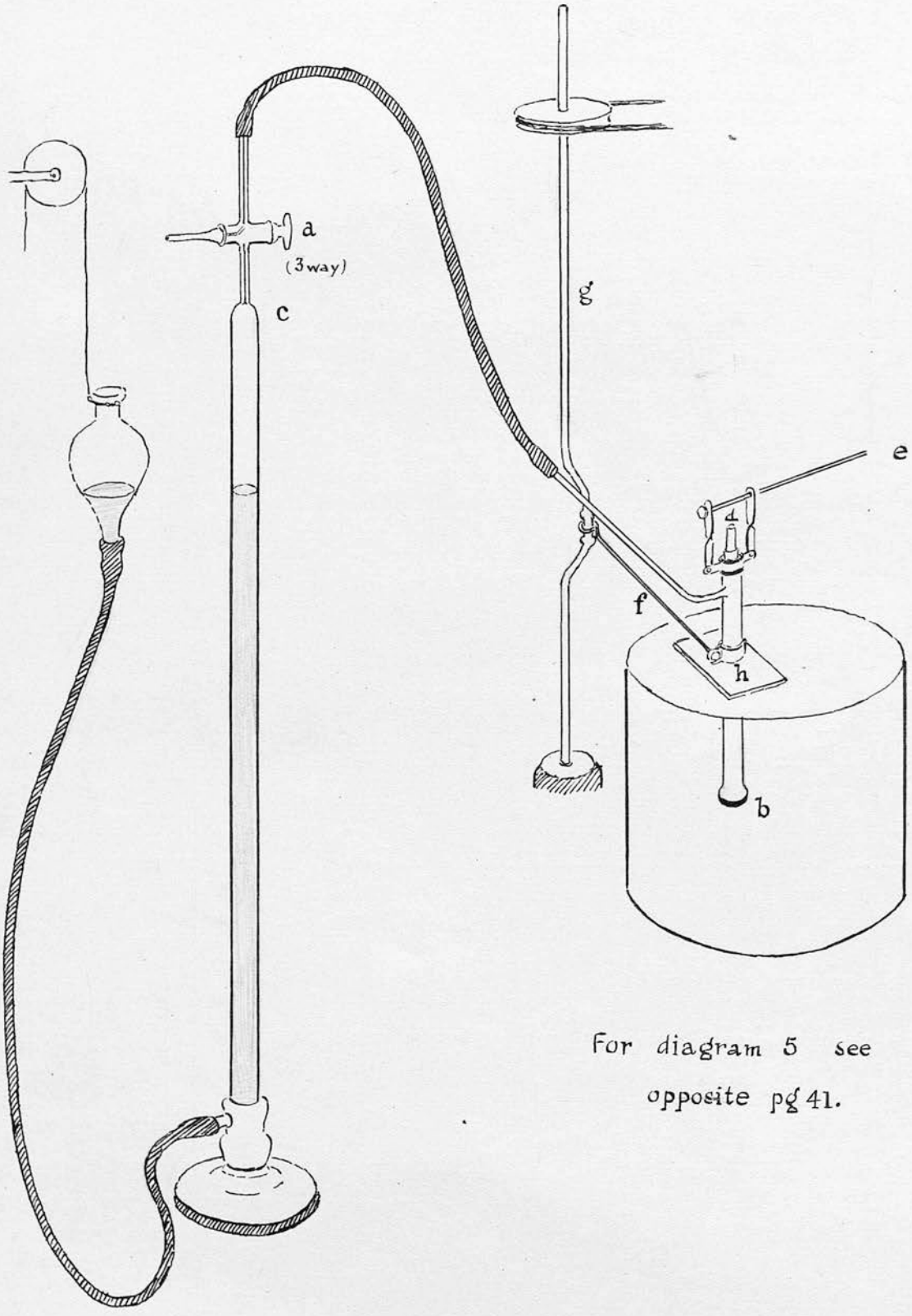
Expt. LXXXVI : Oxalpropionic ester, at 160°C with intermittent stream of CO_2.

$a = \frac{758}{763} \times 26.6 = 26.4$ cc ; log a = 1.4216 ; Take to = 10h. 45 m.
(Atmos. Press. = 763 mm.)

t_1	v *	x	26.4-x	$\log {}^{a}/_{a-x}$		t	x/t
10.41	start	-	-	-		-	-
.56	1.3	1.1	25.3	.0185		11	0.100
11.11	2.4	2.2	24.2	.0378		26	.085
.28	4.3	4.1	22.3	.0733		43	.095
12.0	7.7	7.5	18.9	.145		75	.100
.32	11.4	11.15	15.25	.238		107	.104
1.13	16.2	15.95	10.45	.402		148	.108
2.11	21.3	21.1	5.3	.697		206	.102
3.33	24.6	24.4	2.0	1.121		288	.085
5.13	25.5	25.3	1.1	1·380		388	-
∞	26.8	26.6	(758 mm.)				

Average : $k = 0.097$

DIAGRAM 4.



For diagram 5 see opposite pg 41.

VELOCITY DETERMINATION WITHOUT CARBON DIOXIDE STREAM.

In the experiments described already, a stream of gas has always been used, to take the carbon monoxide out of the solution. The question arises - will the carbon monoxide be formed at the same rate, if we allow it to escape from the solution under its own pressure? We may anticipate that, where a gas is formed in a liquid, a fairly high degree of supersaturation will be necessary, before bubbles appear. Beyond this point, however, the concentration of carbon monoxide in the liquid will remain constant and the evolved gas should, then, give a measure of the rate of decomposition as, for instance does the nitrogen, from aqueous solutions of diazonium salts. Further, if Perrin is correct in assuming that the molecule in a unimolecular decomposition, 'explodes' without reference to its neighbours, then we should expect the rate, measured in this way, to be the same as when carbon dioxide is used. It is true that the results, just quoted, lead to a different expectation and, in fact, make it doubtful whether the unimolecular law will be followed.

The apparatus used is shown in diagrams 4 and 5. In essence, this apparatus depends on the same principle as the Victor-Meyer method of determining molecular/

DIAGRAM 7.

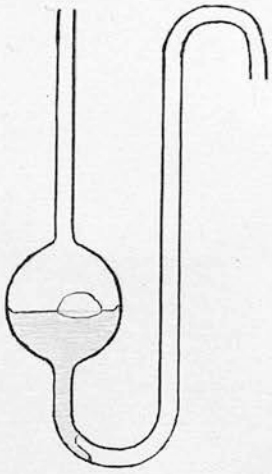
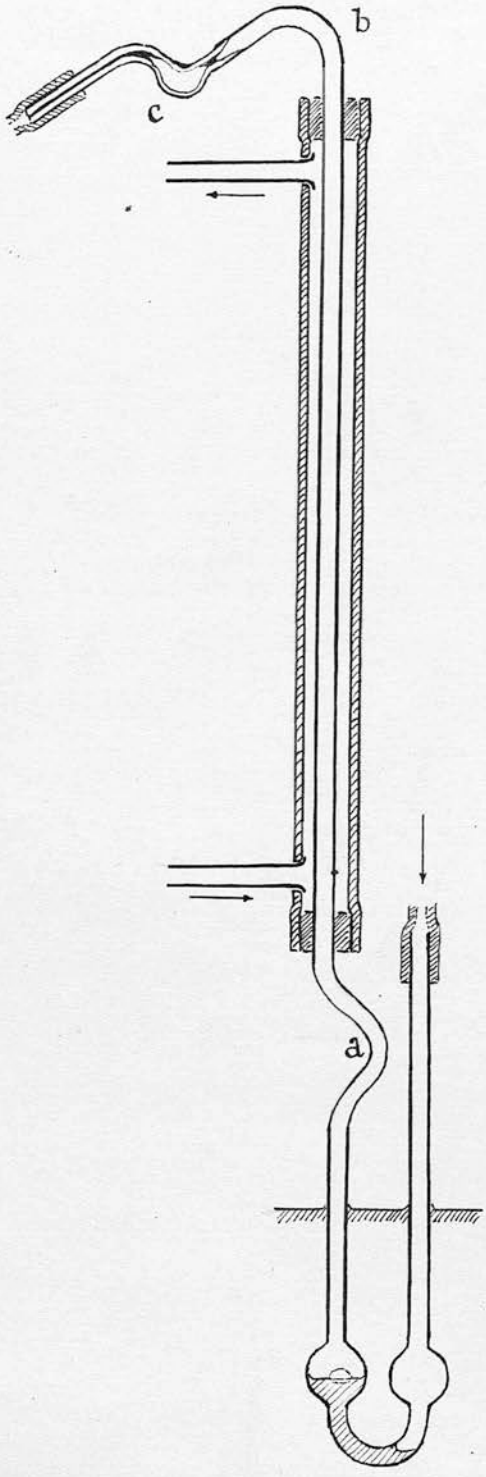


DIAGRAM 6.



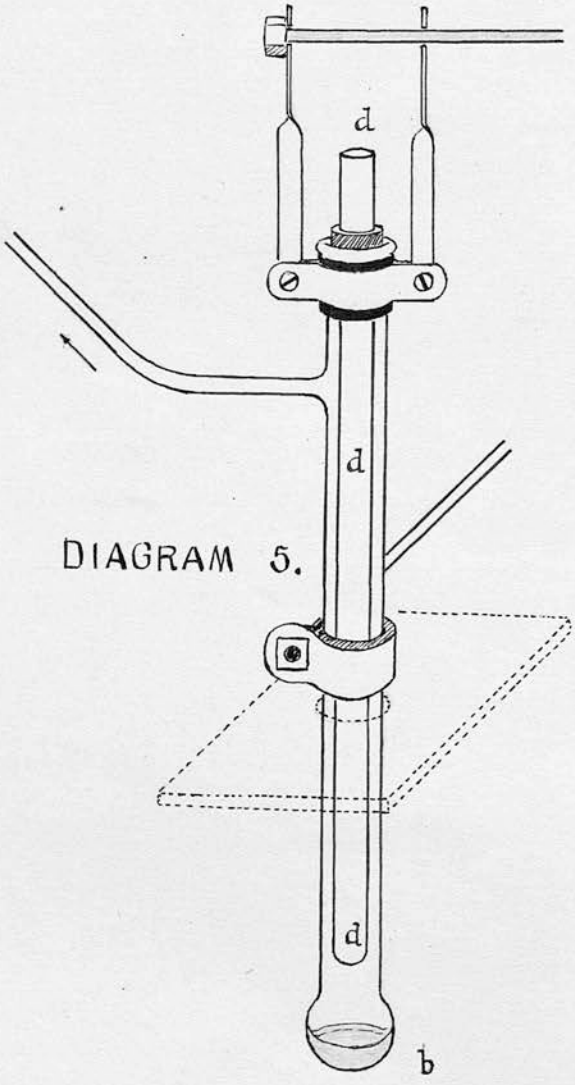


DIAGRAM 5.

molecular weights. The ester in the foot of the tube b ,is kept at the temperature of the bath, while the gas evolved (mixed with the small volume of air, present in the apparatus at the outset) is measured at atmospheric temperature and pressure in the gas burette c. The dead space in the apparatus was kept as small as possible, as shown by the closed tube d, used as a stopper, and by using narrow glass and rubber tubing for the connection to the gas burette.

It was soon evident, that no measurements of value could be obtained, unless the ester were kept in constant motion. The high temperature of the bath and consequent necessity of keeping the internal volume small, made the use of a stirrer impracticable. The tube was, however, kept in rapid agitation by the shaking device shown in the diagram. The tube was fixed, by means of a brass clamp, to a horizontal axle (e) and was thus free to swing, pendulum-fashion, in a plane,perpendicular to the direction of the side-tube. The motion was conveyed to the tube from a rotating vertical shaft (g) by means of the rod (f). The tube passed through a suitably shaped hole in the lid of the bath, and carried a heat-shield of asbestos board (h),which just grazed the lid when the shaker was in action. The rate was about one complete swing per second.

The preliminary experiments were performed with the/

the ethoxy derivative at 190°C. In ~~making~~ the calculations, the gas evolved during the first half-hour was ignored. On calculating the values of $\frac{1}{t} \log \frac{a}{a-x}$, it was at once evident that the velocity was strictly unimolecular. At 190°, however, the average velocity was 151×10^{-4} (Expt. XVI), which shows that the reaction, under these circumstances, is much slower than normally. A previous, and less accurate, experiment gave $k = 140 \times 10^{-4}$.

The method was also used with oxalpropionic ester and as the results in this case can be used to find the temperature variation of the constant, the experiment is tabulated in full. (See table 12, p.44) The first part was done with the bath at 160°C. and the latter part at 170°C. In this experiment the tube at b was filled with small pieces of pumice - with the object of exposing as large a surface of the ester as possible.

As before, we see that the retardation is very marked (Cf. Table 19), but the unimolecular law is certainly obeyed. The temperature coefficient is about 4.5 for a 10° rise or 61,200 cals. This is exceptionally large, being nearly twice the true chemical heat of activation.

It will be remembered that one of the hypotheses brought forward to explain what was called the "slow" reaction, was, that the surface exposed had some effect/

effect on the constant measured. The result just given, shows that we cannot obtain the normal constant by exposing a large surface even with violent shaking. Another experiment, suggested by this theory, was performed with the methyl derivative. The ordinary carbon dioxide method was used but the bulbs of the reaction-tube were half-filled with pieces of pumice, before introducing the substance. These sucked up the ester like a sponge, and enabled it to present a much larger surface, than usual, to the stream of carbon dioxide. The velocity was again unimolecular and had the average value $\underline{71.2 \times 10^{-4}}$. (Expt. LXXXVIII) at 160°C. The average of two normal experiments at 160° (see table 21), is 80.2 and it is thus evident that the velocity is uninfluenced by this change.

(TABLE 12)

TABLE 12.

Expt. XCIX : Oxalpropionic ester, without CO_2 stream.

At 160.0°C : Calculate from 12 h. 40 m. as zero time.

a = 38.6 cc (41.8 - 3.2); log a = 1.5866 ; t_o = 12 h. 40 m.

t_1	v	(41.8-v)	log $^a/_{a-x}$	t	K x 10^4
12.40	3.2	-	-	(t_1 - 12h 40)	-
1.20	4.2	37.6	.0114	40	2.85
2.51	6.6	35.2	.0401	131	3.06
4.10	7.9	33.9	.0564	210	2.69
5.7	8.8	33.0	.0681	267	2.55
7.14	11.4	30.4	.1037	394	2.63
9.12	14.1	27.7	.144	512	2.82
(10.45 Temp raised to 170°C)				Average :	2.77 x 10^{-4}

At 170° : Calculate from 11 h. 50 m. as zero time.

a = 22.8 cc (41.8 - 19.0) ; log a = 1.3579 ; t_o = 11 h. 50 m.

11.50	19.0	22.8	-	(t_1 - 11h 50)	-
12.43	22.3	19.5	.0679	53	12.8
2.31	27.6	14.2	.2056	161	12.8
4.20	31.6	10.2	.349	270	12.9
6.45	35.2	6.6	.538	415	13.0
7.52	36.5	5.3	.634	482	13.2
∞	41.8	-	-	-	-
				Average :	12.94 x 10^{-4}

(N.B. Values of v subject only to a constant difference error).

EXPERIMENTAL PROCEDURE IN LATER MEASUREMENTS.

In using the stream method, to determine the temperature coefficient for this reaction with accuracy, some consideration was given to improving the method of working. The main weaknesses of the experiments already described were: (1) Risk of distillation of ester, if stream of gas were too strong. (2) Variation in temperature of collected gas. (3) Presence of comparatively large amounts of air in the carbon dioxide and (4) Impurities in the ethoxy-ester.

(1) In later experiments the design of the reaction-tube was changed somewhat, as a result of successive improvements, and the final form is shown in diagram 6, pg40a. The bend at a, served to prevent the liquid from spurting up the condenser and allowed the use of a very small opening in the lid of the bath. The upright tube a b was lengthened to 6½ inches and round it was fitted a water-condenser of rubber-tubing. The advantage of this lay in the ease with which it could be affixed, where a glass condenser would be out of the question. When a stream of tap water was passing through this condenser, it was easy to adjust the rate of carbon dioxide so that no droplets of liquid appeared on the exposed glass at b. In case a little malonic ester did pass the condenser/

condenser,an effective trap was provided on the capillary leading tube at (c). This was of small volume and so designed that the carbon dioxide would constantly sweep through it. In most experiments, the amount of liquid collecting here was negligible, compared with the amount of ester used.

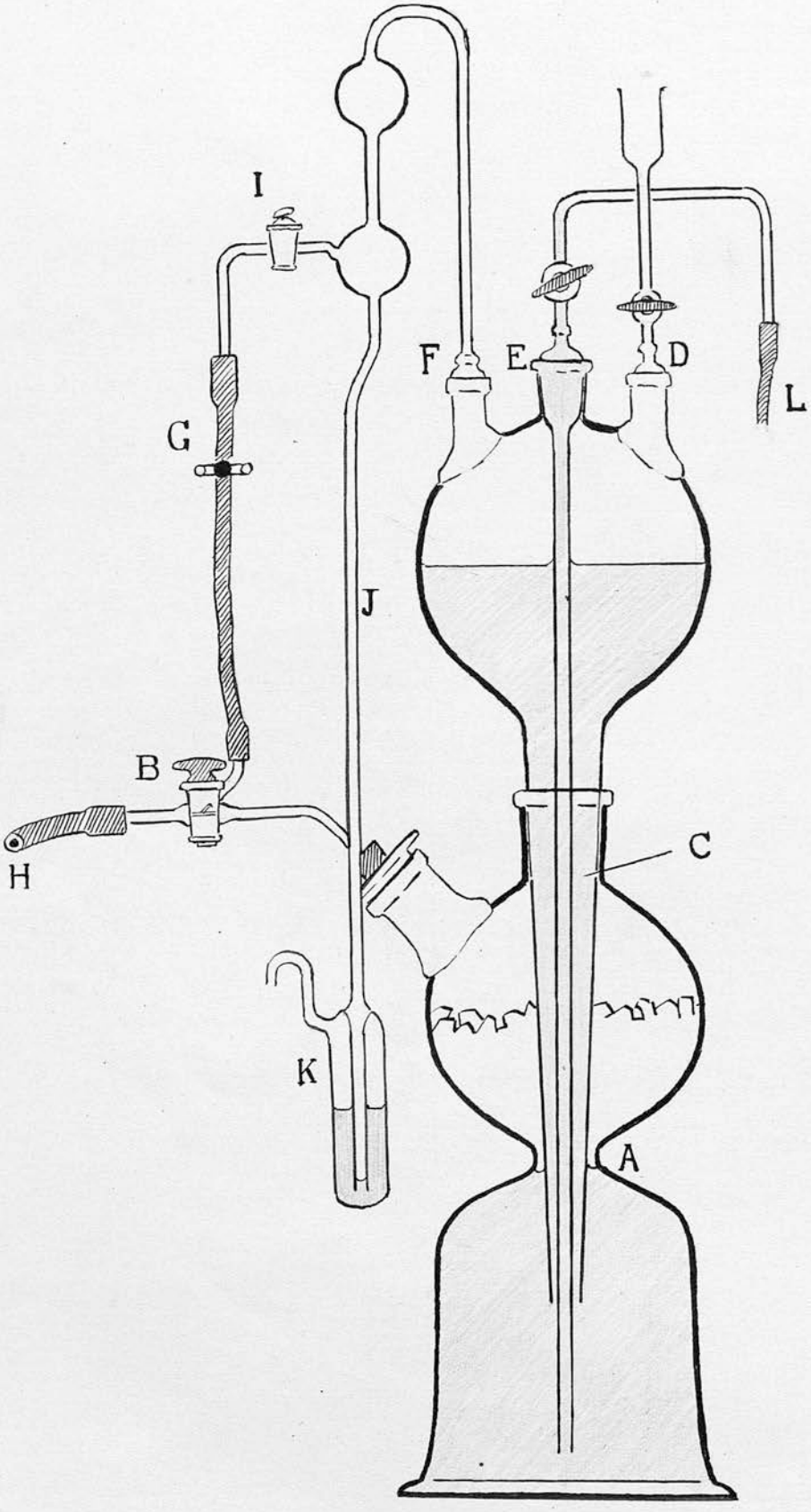
The reaction-tube was connected by pressure tubing to the capillary leading-tube and that, in turn, to the inlet tube of the nitrometer. This inlet, specially fused on, was also of capillary tubing. Under these circumstances, the volume of the system from the surface of the ester to the mercury of the nitrometer could not have been more than 0.5 cc. - 1.0 cc.

With regard to (2), a water-jacket was fitted round the upper half of the nitrometer and through it, a stream of tap-water passed, during the experiment. The temperature of this water did not vary more than half a degree - which is sufficiently constant for our purpose. A thermometer was placed in the jacket.

In these experiments, too, a special type of bubbler (shown in diagram 7, pg403) was used - for washing the carbon dioxide. This had the advantage of being small in volume and of such a shape, that air could be washed out from it, in a very short time. No permanganate was used.

(3)./

DIAGRAM 8.



(3) The carbon dioxide was obtained from a special type of Kipp's apparatus, shown in diagram 8,(opp.). Before charging this apparatus,the marble and hydrochloric acid - both of which contain a considerable amount of air - were specially treated. The marble was first washed with water, dilute hydrochloric acid and again with water. It was then heated for twenty-four hours,on the steam bath,under the suction of the water pump (10 mm. Hg.). At the end of this time, before admitting air, freshly-boiled distilled water was run into the distilling-flask,until the marble was covered. The lower section of the Kipp (to the neck A) was now filled with 1 : 1 hydrochloric acid, which was freed from air by dropping in two or three pieces of marble. The cooled, prepared, marble was now introduced to the centre bulb and the outlet of the three-way tap B, closed. Then the upper bulb was more than half-filled with acid - which was also washed free from air, by placing a nut of marble in the neck C.

The effectiveness of this apparatus depends on two principles. (a) The passage B G I F allows carbon dioxide to pass, from the middle bulb to the top one, and thus an atmosphere of this gas may be maintained above the acid. (b) The outlet tube J and trap K allow carbon dioxide to escape but at the same time,prevent air from entering. If the cock I be opened, the acid will fall into the lower chamber and/

and carbon dioxide will pass into the top bulb. When the acid has reached the marble, the tap I is closed and the gas formed forces the acid back into the upper bulb, at the same time, driving the gas above out into the air, via F J K.

By repetition of these two processes many times, the air, remaining in the apparatus after charging, was removed. After being washed out in this way, the apparatus stood for a day, before using. The carbon dioxide was then allowed to issue steadily for an hour, while the tap I was opened occasionally. If the gas gave bubbles 0.1 mm. in diameter when passed into caustic potash, it was considered ready for use. The tubes D, E and F were connected to the apparatus by ground-glass joins, and the junction B - G was made by rubber tubing. The tube E was used for getting rid of spent acid, from the bottom of the apparatus, without admitting air.

In order to eliminate any remaining <u>oxygen</u> from the gas, a straight tube, containing small pieces of moist phosphorus, was inserted between the "Kipp" and the bubblers. The phosphorus trioxide, formed here, would be absorbed by the bicarbonate.

The thermometer used in the oil-bath was calibrated and found accurate to 0.1°C.

ERRORS OF MEASUREMENT.

Before going on to enumerate the results, it will be instructive to consider how the various errors of method and observation are likely to influence the constant obtained. If we wish to determine the error, produced in the calculated quantity k, by a certain error in one of the measurements, we must differentiate the expression for k, partially, with regard to the variable in question. The function thus obtained is the ratio of the derived error in k, to the error in the variable. (This method has already been applied by Rice & Kilpatrick, (J. Amer. C.S. 45, 1401) to the case of a bimolecular reaction measured by titration methods).

Error in x.

Thus if we differentiate partially

$k_e = \frac{1}{t} \log_e {}^{a}/_{a-x}$, with regard to x, we have

$$\frac{\partial K_e}{\partial x} = + \frac{1}{t} \frac{1}{(a-x)}$$

From what has been said, we may assume that the error in x is of the order of 0.1 cc. ($= \Delta x$). In the following table, the values of x and t from an actual experiment, are given. The average value of k was 0.0146, using logs. to base 10 i.e. $k_e = 2.3 \times .0146$. In the fourth column, instead of the absolute error, we have calculated the fractional error/

error corresponding to an error of 0.1 in x.

$$\text{i.e. } \frac{\Delta k_e}{k_e} = \pm \frac{1}{t} \frac{1}{(a-x)} \times \frac{0.1}{2.3 \times k}$$

For comparison the fractional error in x, $(\frac{\Delta x}{x})$ is also given.

x	t	(a - x)	$\frac{\Delta k}{2.3k}$	$\frac{\Delta x}{x}$
14.2	11	31.2	0.87%	0.7%
29.6	31	15.8	.61	.34
40.2	72	5.3	.80	.25

We may conclude from this, that accuracy of k will not be affected by more than 1%, on account of the error in x.

Error in t.

When we come to consider the systematic error in t, we find that its effect on the value of the constant can also be neglected. By the method of working employed, the error in t should not be more than 3 secs = 0.05 min.

Differentiating $\frac{1}{t} \log {}^{a}/_{a-x}$ partially with regard to t, we have:

$$\Delta k = -\frac{1}{t^2} \log {}^{a}/_{a-x} \cdot \Delta k = -\frac{k}{t} \cdot \Delta t$$

$$\text{i.e. } \frac{\Delta k}{k} = -\frac{\Delta t}{t} = \frac{.05}{10}$$ after ten minutes
i.e. 0.5%

As the error in k due to t, thus varies inversely as t, it will become less and less as the experiment proceeds.

Error in a.

The chief factor causing an error in a will be the presence of air in the carbon dioxide. In the experiment used for calculation already, where a = 45.5 cc, let us assume that the air is present to the extent of 1 cc., i.e. about 2% error in a.

$$k_{10} = \cdot\frac{434}{t} \log_e \frac{a}{a-x}$$

i.e. $$\frac{\partial k_{10}}{\partial a} = \cdot\frac{434}{t}\left(\frac{1}{a} - \frac{1}{a-x}\right) = -\frac{\cdot 434\ x}{at\ (a-x)}$$

Using the same experimental results : $k_{10} = .0146$.

t	x	(a-x)	$\frac{\cdot 434\ x}{at\ (a-x)}$	$\frac{\Delta k_{10}}{k_{10}}$ ($\Delta a = 1$ cc)
11	14.3	31.2	- .00040	- 2.7%
21	23.0	22.5	46	3.1
31	29.7	15.8	58	4.0
38	33.0	12.4	67	4.6
56	38.2	7.3	89	6.1
			Av.	4.1%

Thus, on the average, the fractional error produced in the constant is twice that originally present in a. The calculation enables us to see why comparatively large amounts of air, in the early experiments, do not interfere very seriously with the trustworthiness of the constant, especially when we take into account the argument, already put forward, for not correcting the values of x for air. In later experiments/

experiments the amount of nitrogen measured afterwards was of the order of 0.5 cc. and in this case the derived error in the constant will be nearer 2%.

TEMPERATURE COEFFICIENTS.

OXALACETIC ESTER.

Wislicenus was able, by very careful heating, to convert this ester largely into malonic ester and carbon monoxide. (Ber. 27, 792). Normally, however, he found that another type of reaction proceeded simultaneouly - as already described. It was hoped here, in spite of the latter side-reaction, to measure the velocity with sufficient accuracy to determine the temperature coefficient.

An experiment was first performed to obtain an estimate, as to the extent of the side-reaction. Our preparation was freshly distilled and decomposed at 175°C. The residue at the finish was an extremely viscous oil, like that obtained on redistillation, and the yield of carbon monoxide was less than one-half of the theoretical.

A velocity determination was then carried out at 165.0°C, by the method just described in detail. The results are shown in table 13, p. 61 .

It/

It is quite certain from these, that, even though the side-reaction is so marked, the carbon-monoxide decomposition is again unimolecular. A fair amount of liquid distilled in the course of the experiment - probably pyruvic ester and alcohol.

In view of the extent of the condensation reaction, in the case of this substance, it was decided not to measure the temperature variation of the constant.

ETHOXY-OXALACETIC ESTER.

The experiments, carried out with this ester, in order to determine the effect of temperature, fall into two groups. In the first, the velocity was measured at intervals of 5° in the region between 173° and 198°, primarily with the object of testing the truth of the Arrhenius law. Here, the experimental procedure was still in course of development, and it was not surprising, on repeating the measurements by the more accurate method, that differences were found at higher temperatures. (pages 62:63) The results of the two sets of experiments are tabulated in table 16. pg75.

On integrating the Arrhenius equation:

$$\frac{d}{dt} (\log. K) = \frac{Q}{RT^2} \qquad (1)$$ we obtain

$$\log_{10} K = - \frac{Q}{2.3RT} + B \qquad (2)$$

Thus, if this law is followed there should be a linear relation between $\log_{10}K$ and $1/T$. These two quantities/

quantities are plotted in Graph IV, pg74a- K being the average value for the temperature T (see table 16).

Except at the higher temperatures, the points lie close to a straight line and we may conclude that the Arrhenius law is followed. The discrepancy of the values at 193° and 198°C. is probably connected with the disturbing secondary reaction. The points corresponding are therefore ignored in calculating the temperature coefficient.

If the Arrhenius equation be integrated between temperatures T_1 and T_2 we have

$$\log_{10} \frac{K_1}{K_2} = \frac{Q}{2.3\ R} \frac{T_1 - T_2}{T_1 T_2} \qquad (3)$$

Using the values (2) and (4),(which lie close to the line on the graph) with this equation, and value (3) in equation (2) we obtain :

$$\begin{cases} Q = 35{,}800 \text{ cals} \\ B = 13.94 . \end{cases}$$

The exact method of calculation will be illustrated later with oxalpropionic ester.

OXALPROPIONIC AND OXALSUCCINIC ESTERS.

The experiments with these compounds - likewise with the phenyl derivative - were carried out by the later method as described on p. 45 . The principle was adopted, of repeating the measurement at each temperature/

temperature until two results in good agreement, were obtained. Of the two experiments, only one at each temperature is given in full in the tables 17 to 24. The second result is given along with this in the tables 21 and 25, (pgs. 76 & 77) which summarise all the velocity determinations with the two compounds. In these tables, are also given, the data necessary for graphically testing the law of Arrhenius: i.e. $^1/_T$ and $\log_{10}(K \times 10^4)$, whose values are plotted in the two graphs V (pg. 74a) and VI (pg. 76a). For this purpose of course, the velocity must be known at, at least, three different temperatures.

In all the experiments, it appears that the unimolecular law is a very good approximation to the truth. In fact, with both substances the agreement at the end of the experiment, is distinctly better than in the case of ethoxy-oxalacetic ester. Further, there is no doubt from the graphs but that the Arrhenius law holds good. The values of Q and B in this case were found to be : -

Oxal-propionic : Q = 33,300 cals, B = 13.36)
" succinic : Q = 35,400 " , B = 14.30)

- not far removed from those for the ethoxy compound.

The calculation was as follows for oxalpropionic ester:

The graph shows that the points, represented by the average values of K , at 150° and 165°, lie on the/

the straight line. These are given ~~at the foot of~~ in table 21.

$$\text{Now } Q = \frac{R\ T_1\ T_2\ (\log_{10}K_1 - \log_{10}K_2)\ 2.302}{(T_1 - T_2)}$$

$$= \frac{1.985 \times 438 \times 423 \times 0.592 \times 2.303}{15.0} = \frac{33.300}{} \text{ cals}$$

For exalsuccinic ester, the average values at 150° and 170° were used in the same way. (Table 25).

To calculate B , we use this value of Q along with the average absolute value of K at 165°C. Now K is expressed in minutes $^{-1}$ and logarithms to the base 10. i.e.

$$\log_{10}K_{abs} = \frac{119.3 \times 2.3 \times 10^{-4}}{60} = \bar{4}.66.$$

$$\frac{Q}{2.3\ RT} = \frac{33,300}{2.302 \times 1.985 \times 438} = 16.70$$

Now from (2) above

$$B = 16.70 + \bar{4}.66 = \underline{13.36}$$

For oxalsuccinic ester, the average value of K at 170° was used in exactly the same way.

PHENYLOXALACETIC ESTER.

In the section devoted to preparation, it has been mentioned that great difficulty was experienced in distilling this substance. The distillate, obtained with/

with the help of a Gaede pump, was so much decomposed during the heating, that it contained only 28 per cent of the substance - the rest being phenyl malonic ester, formed by loss of carbon monoxide. This preparation was used for a velocity determination at 160°C and found to obey the first order law, with great accuracy (see table 28). However, when the rich, undistilled preparation was used (at 150°C) the values of $\log {}^{a}/_{a-x}$ did not vary linearly with $\underline{t}$, but increased much more rapidly - the graph of $\log {}^{a}/_{a-x}$ against t, being a smooth curve resembling a parabola, convex towards the $\underline{t}$-axis.

Thus, we may look on the unimolecular velocity as getting faster as the experiment proceeds. If we are to find a differential equation to express this fact, the simplest assumption to make is, that at any instant, the velocity, besides being proportional to the number of reacting molecules, is proportional to number of phenyl-malonic-ester-molecules formed.

$$\text{i.e.} \quad \frac{d\underline{x}}{dt} = k.x.(a-x) \qquad (4)$$

- which represents an "auto-catalytic" reaction.
On integration, this equation gives

$$\log \frac{x}{a-x} = akt + \text{const.} \qquad (5)$$

and if we consider the point where the reaction has gone half way,

$$x = {}^{a}/_{2} \quad \text{and} \quad t = t_{\frac{1}{2}}.$$

Then, const. $= - akt_{\frac{1}{2}}$

$$\text{and } k = \frac{1}{a\,(t - t_{\frac{1}{2}})} \log \frac{x}{(a-x)} \qquad (6)$$

The values of experiment CV were used in this formula and the constancy of k , throughout the whole experiment, was so good as to establish without doubt, that this, indeed,is the equation of the reaction.

There is, however, another solution of the above equation, i.e.

$$k = \frac{1}{at} \log \frac{ax}{a-x} \qquad (7)$$

This has been used in table 30 (pg.74) to calculate the values of the velocity constant k for expt. CV. The first three columns there,are familiar. The values of $\log \frac{ax}{a-x}$ in the next column, were plotted against t_1 and found to give a straight line. This was produced to meet the line $\log \frac{ax}{a-x} = 0$, and the value t_o obtained, which represents the zero time of the reaction, for the purposes of this calculation. It should be noted that this is a mathematical device, for, strictly speaking, the reaction will not start, unless there is present, at least a trace of the products. This is the reason that t_o is found earlier, than the observed "start" of the reaction.

In the last column, it will be seen that the values/

values of $\frac{1}{t} \log \frac{ax}{a-x}$ $(= ak)$ are remarkably constant - not even the first or last reading being appreciably exempt. Another experiment, (CII) under the same conditions, showed a similar consistency, though the absolute value was smaller ($k = \underline{45.7}$ instead of 48.7×10^{-5}). We are therefore entitled to say that the decomposition of phenyloxalacetic ester - under these conditions - is autocatalytic and of the first order.

How, then, are we to explain the unimolecular constant obtained with the dilute preparation? In this case, we are really separating out and examining a small portion at the end of the whole reaction. Now, even with experiment CV, it was possible to choose a value of t_o which made $\frac{1}{t} \log \frac{a}{a-x}$ constant for the last four of five readings, so there is really nothing surprising about this fact. At this part of the experiment, the values of $(a - x)$ are changing much more rapidly than $\underline{x}$, and the equation

$$\frac{dx}{dt} = k_1 x (a-x)$$ is thus reverting to

$$\frac{dx}{dt} = k_2 (a-x)$$

At this point, $\underline{x}$ is approaching $\underline{a}$ and therefore, $k_2 \longrightarrow k_1 a$. That this is indeed the case, is beautifully demonstrated when we compare the constant $k_1 a$ of expt. CV (196) with the unimolecular constant of experiment CVI (186), which was done with the/

the dilute preparation, at the same temperature, (Table 27).

Thus, in examining the "apparent" unimolecular constant of the decomposition of the dilute preparation, we are, indirectly, measuring the true autocatalytic constant. Hence the temperature coefficient has been examined, as before, and the results of experiments at 140°, 150° and 160°C are given in full on tables 26-28, and summarised in table 29, p. 77. The constancy of the unimolecular constant is, in each case, very good as is also the agreement with the Arrhenius law-shown by the straight line in graph VII. Using the method already described, we find from this line,

$$Q = 44{,}300 \text{ cals.}$$
$$B = 19.88$$

The net result of the effect of temperature on the velocity of dissociation, as we pass from one compound to another will be found in table 31, p. 78. Here are given, besides Q and B, the derived values of the Lewis-Perrin wave-length (which are used in the next section) and the "active-life", (which is referred to in the discussion of results).

TABLE 13.

EXPT. LXXXIX : OXALACETIC ESTER AT 165°C.

a = 8.55 cc. log a = 0.9320 , t_o = 11 h. 36 m.

t_1	v	c	x	8.55-x	log $^a/_{a-x}$	t	K x 10^4
11.19	Start	-	-	-	-	-	-
.43	1.6	0.35	1.25	7.3	0.0687	7	(98)
12.3	3.25	.5	2.75	5.8	.1686	27	62.5
.37	5.9	.75	5.15	3.4	.401	61	65.8
1.23	7.7	.9	6.8	1.75	.689	107	64.3
3.24	9.4	1.05	8.35	0.2	1.631	228	71.5
∞	9.6	1.05	8.55	-	-	-	-

Average : $k = 65.9 \times 10^{-4}$

TABLE 14.

Expt. LXXVI : Ethoxy-oxalacetic ester at 173.0°C.

a = 31.0 cc ; $\log_a$ = 1.4914 ; t_o = 11 h. 5.2 m.

t_1	v	c	x	31.0-x	log $^a/_{a-x}$	t	K x 10^4
11.4	start	-	-	-	-	-	-
.10	2.4	0.45	1.95	29.05	.0283	4.8	(59)
.16	4.4	.65	3.75	27.25	.0560	10.8	51.8
.25	7.3	.9	6.4	24.6	.1005	19.8	50.7
.35	10.2	1.1	9.1	21.9	.1510	29.8	50.7
.45	12.8	1.3	11.5	19.5	.2014	39.8	50.7
12.1	16.4	1.6	14.8	16.2	.282	55.8	50.6
.17	19.5	1.8	17.7	13.3	.367	71.8	51.2
.33	22.1	1.9	20.2	10.8	.458	87.8	52.2
1.13	26.5	2.15	24.35	6.65	.669	127.8	52.3
3.13	30.3	2.3	28.0	3.0	1.014	247.8	(41)
∞	33.5	2.5	31.0	-	-	-	-

Average : $k = 51.3 \times 10^{-4}$

TABLE 15.

Expt. LXXV : Ethoxy-oxalacetic ester at 193.0°C.

a = 34.0 cc ; log a = 1.5315 ; t_o = 11 h. 25.6 m.

t_1	v	c	x	34.0-x	log $^{a}/_{a-x}$	t	K x 10^4
11.24	start	-	-	-	-	-	-
.29	7.8	0.9	6.9	27.1	.0985	3.4	(290)
.31	10.8	1.2	9.6	24.4	.1441	5.4	267
.34	14.8	1.5	13.3	20.7	.2155	8.4	257
.37	18.4	1.75	16.65	17.3	.292	11.4	257
.40	21.4	1.85	19.55	14.45	.372	14.4	258
.44	24.7	2.05	22.65	11.3	.477	18.4	260
.49	27.4	2.2	25.2	8.8	.587	23.4	251
.55	29.7	2.3	27.4	6.6	.712	29.4	242
12.10	31.7	2.4	29.3	4.7	.859	44.4	(193)
2.45	34.2	2.5	31.7	2.3	1.170	199.4	(59)
∞	36.6	2.6	34.0	-	-	-	-

Average $k = 256.0 \times 10^{-4}$

TABLE 17.

Expt. LXXXI : Oxalpropionic ester at 150.0°C.

a = 42.0 cc ; $\log_a$ = 1.6232 ; t_o = 10 h. 58 m.

t_1	v	c	x	42.0-x	$\log {}^{a}/_{a-x}$	t	K x 10^4
10.45	start	-	-	-	-	-	-
.18	7.5	0.9	6.6	35.4	.0742	20	(37.1)
.30	10.6	1.15	9.45	32.55	.1106	32	(34.5)
.45	13.7	1.4	12.3	29.7	.1504	47	32.0
.59	16.4	1.6	14.8	27.2	.1886	61	30.9
12.18	19.8	1.8	18.0	24.0	.243	80	30.4
.37	23.1	1.95	21.1	20.85	.304	99	30.7
1.2	26.9	2.2	24.7	17.3	.385	124	31.1
.30	30.6	2.35	28.2	13.75	.485	152	31.9
1.55	33.1	2.5	30.6	11.4	.566	177	32.0
2.39	37.0	2.6	34.4	7.6	.742	221	33.6
3.44	40.7	2.7	38.0	4.0	1.021	286	(35.7)
∞	44.7	2.7	42.0				

Average: $k = 31.6 \times 10^{-4}$

TABLE 18.

Expt. LXXVII : Oxalpropionic ester at 155.0°C.

$a = 45.8 \times \frac{279}{278} \times \frac{765}{761} = 46.2$ cc ; $\log a = 1.6646$; $t_o = 11$ h 21 m.

(Gas volumes at 6° and 761 mm.)

t_1	v	c	x	46.2-x	$\log {}^{a}/_{a-x}$	t	K x 10^4
11.13	start	-	-	-	-	-	-
.30	6.2	0.8	5.4	40.8	.0539	9	(60)
.37	9.2	1.0	8.2	38.0	.0848	16	53.0
.45	12.5	1.3	11.2	35.0	.1205	24	50.2
.56	16.7	1.6	15.1	31.1	.172	35	49.2
12.7	20.6	1.8	18.8	27.4	.227	46	49.2
.18	24.3	2.0	22.3	23.9	.286	57	50.2
.30	28.0	2.2	25.8	20.4	.355	69	51.4
.45	32.0	2.4	29.6	16.6	.444	84	53.0
1.4	36.1	2.55	33.55	12.65	.562	103	54.5
.23	39.3	2.65	36.65	9.55	.685	122	(56.2)
2.37	45.4	2.8	42.6	3.6	1.108	196	(56.6)
∞	48.6	2.8	45.8*				

(* At 5°C and 765 mm.)

Average: $k = 51.3 \times 10^{-4}$

TABLE 19.

Expt. LXXIX : Oxalpropionic ester at 160°C.

$a = 41.7 \times \frac{734}{760} = 40.2$ cc ; $\log a = 1.6042$; $t_o = 11$ h. 43 m.

(Gas volumes at 5°C and 760 mm.)

t_1	v	c	x	40.2-x	$\log a/a-x$	t	K x 10^4
11.30	start	-	-	-	-	-	-
.45	6.4	0.8	5.6	34.6	.0651	2	(325)
.54	10.6	1.15	9.45	30.75	.1164	11	(106)
12.4	15.0	1.5	13.5	26.7	.1777	21	84.7
.15	19.7	1.8	17.9	22.3	.256	32	80.0
.27	24.4	2.0	22.4	17.8	.354	44	80.5
.41	28.9	2.25	26.65	13.55	.472	58	81.5
.58	33.2	2.5	30.7	9.5	.626	75	83.5
1.21	36.7	2.6	34.1	6.1	.819	98	83.6
2.16	40.5	2.7	37.8	2.4	1.224	153	80.1
5.0	42.5	2.7	39.8	0.4	2.002	317	(63)
∞	44.5	2.8	41.7*				

(* At 5°C and 734 mm.)

Average: $k = 82.0 \times 10^{-4}$

TABLE 20.

Expt. LXXXII : Oxalpropionic ester at 165°C.

a = 30.8 cc ; $\log_a$ = 1.4886 ; t_o = 11 h. 9.5 m.

t_1	v	c	x	(30.8-x)	log $^{a}/_{a-x}$	t	K x 10^4
11.3	start	-	-	-	-	-	-
.11	3.8	0.6	3.2	27.6	.0477	1.5	(318)
.17	7.4	.9	6.5	24.3	.1030	7.5	(138)
.22	10.4	1.1	9.3	21.5	.1562	12.5	125.0
.29	14.3	1.4	12.9	17.9	.236	19.5	121.0
.38	18.7	1.75	16.95	13.85	.347	28.5	122.0
.47	22.2	1.9	20.3	10.5	.467	37.5	124.8
.58	25.3	2.1	23.2	7.6	.608	48.5	125.2
12.16	28.4	2.25	26.15	4.65	.821	66.5	123.5
.35	30.2	2.3	27.9	2.9	1.026	85.5	120.0
1.39	32.1	2.4	29.7	1.1	1.447	149.5	(97)
∞	33.3	2.5	30.8				

Average : $k = 123.1 \times 10^{-4}$

TABLE 22.

Expt. XC : Oxalsuccinic ester at 150.0°C.

$a = 26.4 \times \frac{750}{744} = 26.6$ cc ; $\log_a = 1.4249$; $t_o = 10$ h. 44 m.

(Gas volumes at 744 mm.)

t_1	v	c	x	26.6-x	$\log {}^{a}/_{a-x}$	t	K x 10^4
10.41½	start	-	-	-	-	-	-
11.6	3.6	0.6	3.0	23.6	.0520	22	(23.6)
.32	5.6	.75	4.85	21.75	.0874	48	18.22
12.1	8.3	1.0	7.3	19.3	.1393	77	18.10
.32	10.8	1.2	9.6	17.0	.1945	108	18.03
1.12	13.5	1.4	12.1	14.5	.263	148	17.77
2.39	17.9	1.7	16.2	10.4	.408	235	17.36
3.45	20.8	1.8	19.0	7.6	.544	301	18.10
5.4	23.2	1.95	21.25	5.3	.696	380	18.32
7.20	25.7	2.1	23.6	3.0	.948	516	18.37
10.50	27.6	2.2	25.4	1.2	1.346	726	18.55
∞	28.7	2.3	26.4 *				

(* At 750 mm.)

Average : $k = 18.09 \times 10^{-4}$

TABLE 23.

Expt. XCI : Oxalsuccinic ester at 160.0°C.

a = 28.7 cc ; $\log_a$ = 1.4579 ; t_o = 10 h. 59.2 m.

t_1	v	c	x	28.7-x	$\log {}^{a}/_{a-x}$	t	K x 10^4
10.57	start	-	-	-	-	-	-
11.12	5.8	0.75	5.05	23.65	.0841	12.8	(65.7)
.21	8.3	1.0	7.3	21.4	.1275	21.8	58.4
.33	11.5	1.2	10.3	18.4	.193	33.8	57.2
.47	14.8	1.5	13.3	15.4	.270	47.8	56.5
12.3	17.9	1.7	16.2	12.5	.361	63.8	56.6
.43	23.6	2.0	21.6	7.1	.607	103.8	58.4
1.19	26.5	2.15	24.35	4.35	.819	139.8	58.4
2.39	29.3	2.3	27.0	1.7	1.227	219.8	55.9
5.7	30.5	2.35	28.15	0.55	2.717	367.8	(74)
∞	31.1	2.4	28.7				

Average : $k = 57.3 \times 10^{-4}$

TABLE 24.

Expt. XCVI : Oxalsuccinic ester at 170.0°C.

$a = \frac{740}{747} \times 21.4 = 21.2$ cc ; $\log_a = 1.3263$; $t_o = 11$ h. 38.7 m.

(Gas volumes at 747 mm.)

t_1	v	c	x	21.2-x	$\log {}^{a}/_{a-x}$	t	K x 10^4
11.34	start	-	-	-	-	-	-
.46	5.6	0.7	4.9	16.3	0.1141	7.3	(156)
.51	7.9	0.9	7.0	14.2	.1740	12.3	141.3
12.0	11.7	1.2	10.5	10.7	.297	21.3	139.6
.7	14.1	1.4	12.7	8.5	.397	28.3	140.3
.17	16.6	1.6	15.0	6.2	.534	38.3	139.6
.31	19.1	1.8	17.3	3.9	.735	52.3	140.5
.53	21.1	1.85	19.25	1.95	1.036	74.3	139.5
2.12	22.6	1.9	20.7	0.5	1.627	153.3	(106)
∞	23.3	1.9	21.4*				

(* At 740 mm.)

Average: $k = 140.1 \times 10^{-4}$

TABLE 26.

Expt. CVII : Phenyl oxalacetic ester at 140.0°C. (25%)

a = 16.0 cc ; $\log_a$ = 1.2041 ; t_o = 11 h. 20 m.

t_1	v	c	x	16.0-x	log $^a/_{a-x}$	t	K x 10^4
11.13	start	-	-	-	-	-	-
.34	2.8	0.5	2.3	13.7	.0674	14	48.2
.48	5.1	.7	4.4	11.6	.1396	28	49.8
.57	6.4	.8	5.6	10.4	.1871	37	50.6
12.16	8.6	1.0	7.6	8.4	.280	56	50.0
.41	10.85	1.15	9.7	6.3	.405	81	50.0
1.13	12.9	1.3	11.6	4.4	.561	113	49.6
2.48	15.9	1.55	14.35	1.65	.987	208	(47.5)
∞	17.7	1.7	16.0				

Average : $k = 49.7 \times 10^{-4}$

TABLE 27.

Expt. CVI : Phenyloxalacetic ester at 150.0°C. (25%)

a = 10.8 cc ; $\log_a$ = 1.0334 ; t_o = 11 h. 5.7 m.

t_1	v	c	x	10·8-x	log $^a/_{a-x}$	t	K x 10^4
11.3	start	-	-	-	-	-	-
.12	3.1	0.5	2.6	8.2	.1196	6.3	190.2
.18	5.1	.7	4.4	6.4	.227	12.3	184.5
.26	7.2	.9	6.3	4.5	.380	20.3	187.3
.35	8.7	1.0	7.7	3.1	.542	29.3	185.0
.59	10.8	1.15	9.65	1.15	.973	53.3	182.5
1.1	11.7	1.25	10.45	0.35	1.489	115.3	(139)
∞	12.1	1.3	10.8				

Average : k = 185.9 x 10^{-4}

TABLE 28.

Expt. CI : Phenyloxalacetic ester at 160°C. (25%)

a = 17.5 cc ; $\log_a$ = 0.2430 ; t_o = 7.45 m.

t_1	v	c	x	17.5-x	$\log {}^{a}/_{a-x}$	t	K x 10^3
12.5	start	-	-	-	-	-	-
.8	3.7	0.6	3.1	14.4	.0846	0.55	(154)
.10	6.7	0.8	5.9	11.6	.1785	2.55	(70)
.12	9.2	1.0	8.2	9.3	.2745	4.55	60.4
.14	11.6	1.2	10.4	7.1	.392	6.55	59.9
.16	13.7	1.35	12.35	5.15	.531	8.55	62.2
.19	15.8	1.55	14.25	3.25	.731	11.55	63.2
.24	17.4	1.65	15.75	1.75	1.000	16.55	60.5
.30	18.4	1.7	16.7	0.8	1.340	22.55	59.5
∞	19.3	1.8	17.5				

Average : $k = 60.9 \times 10^{-3}$

TABLE 30.

Expt. CV : Pure phenyl-oxalacetic ester at 150°C.

(not distilled)

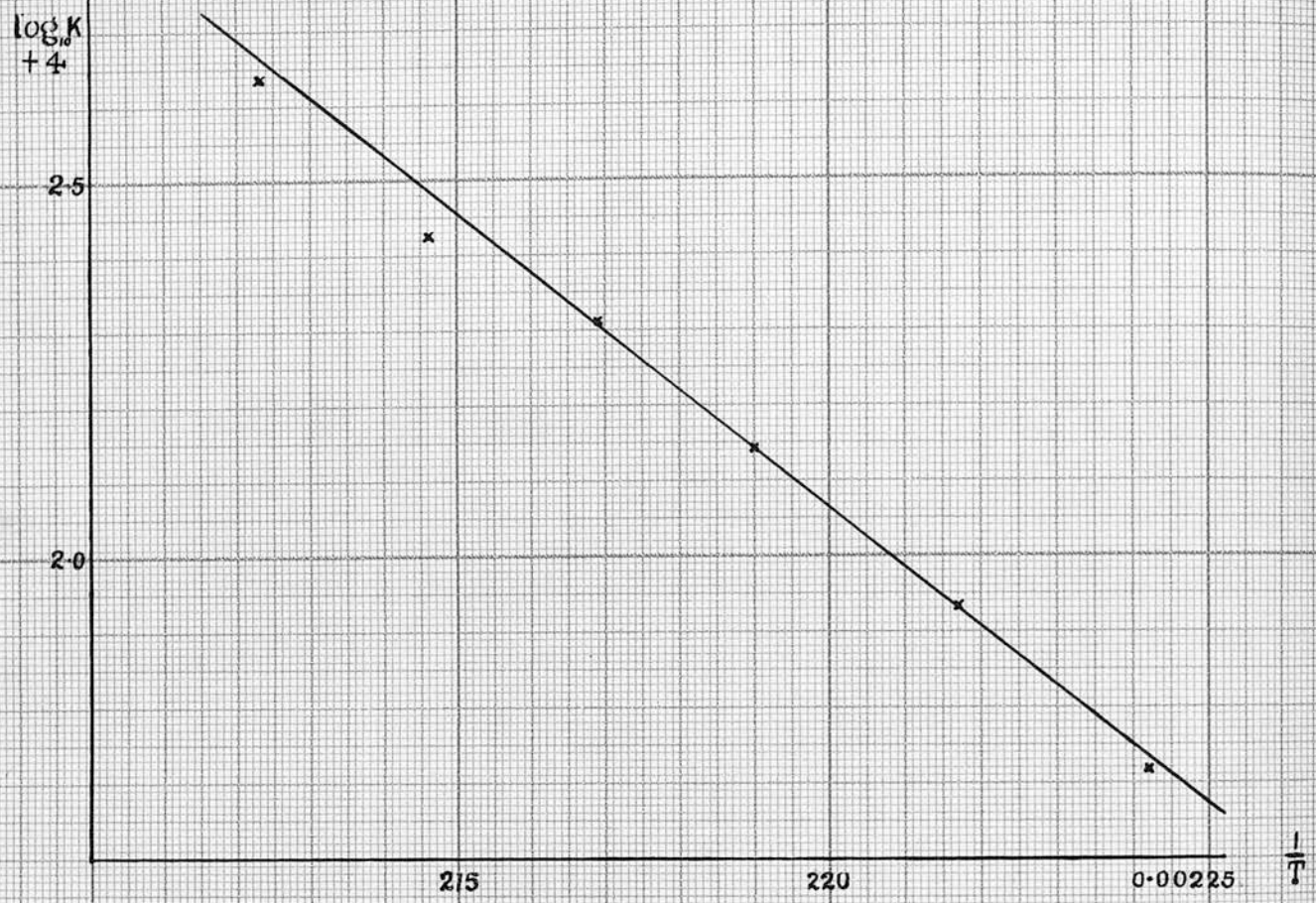
a = 40.3 cc ; log a = 1.6053 ; t_o (from graph) = 2 h. 37 m.

t_1	v	x	$\log \frac{ax}{a-x}$	t_1 - 2.37	$\frac{1}{t} \log \frac{ax}{a-x} \times 10^4$
2.46	start	-	-	-	-
3.9	4.4	3.8	0.623	32	194.5
.24	8.0	7.05	0.932	47	198.5
.36	12.1	10.85	1.172	59	199.
.47	16.5	14.9	1.374	70	196.5
.52	19.3	17.5	1.490	75	199.
.59	22.2	20.3	1.612	82	197.
4.6	25.5	23.4	1.747	89	196.5
.13	28.2	26.0	1.865	96	194.5
.21	31.3	28.9	2.009	104	193.5
.29	34.1	31.6	2.165	112	193.5
.40	37.2	34.6	2.388	123	194.5
.59	40.5	37.8	2.785	142	196.
5.31	42.1	39.4	3.247	174	(187)
∞	43.0	40.3			

Average : $ak = 196.1 \times 10^{-4}$

i.e. $\underline{\underline{k = 48.7 \times 10^{-5}}}$

GRAPH IV. ETHOXY-OXACETIC ESTER.



GRAPH V. OXALPROPIONIC ESTER.

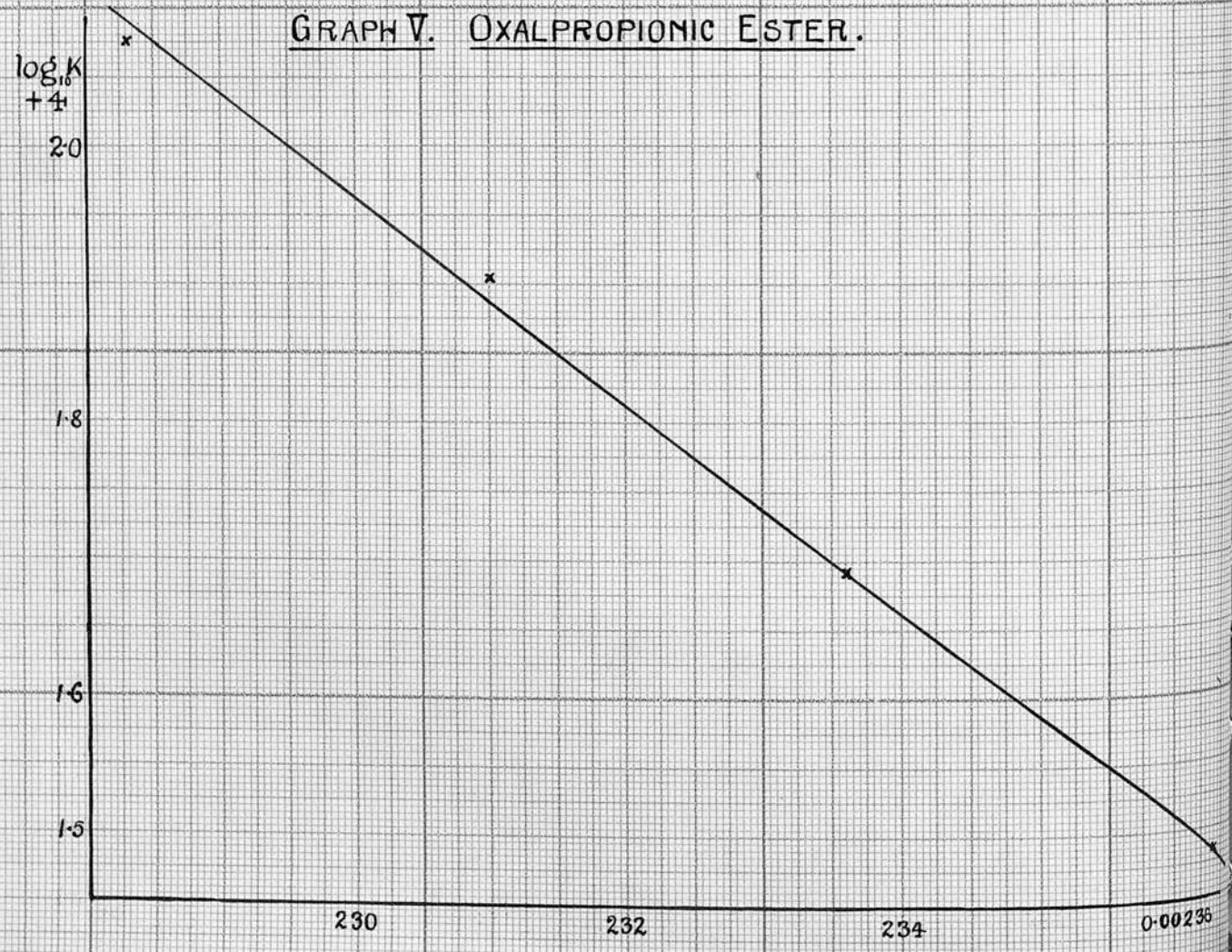


TABLE 16.

Temperature Coefficient for Ethoxy-oxalacetic ester.

(see Graph IV)

Expt.	T^{o} abs.	$K \times 10^{4}$		$1/T$	$\log_{10} K + 4$	
		I	II			
XLIII	446	54.2	-	-	-	
LXXVI pg.62.	"	-	51.3	-	-	
Average	"	52.4	-	.002242	1.719	(1)
XLII	451	85.5	-	2217	1.932	(2)
Aver.table 9	456.5	138.9	-	-	-	
LXXIII	"	-	138.2	-	-	
Average.	"	138.5	-	2190	2.141	(3)
XLIV	461	204.1	-	2169	2.310	(4)
LXV	466	296	-	-	-	
LXXV pg.63.	"	-	256	-	-	
LXXXVII	"	-	247	-	-	
(Average	"	266	-	2146	2.425)	(5)
(XLVI	471	433	-	2123	2.636)	(6)

TABLE 21.

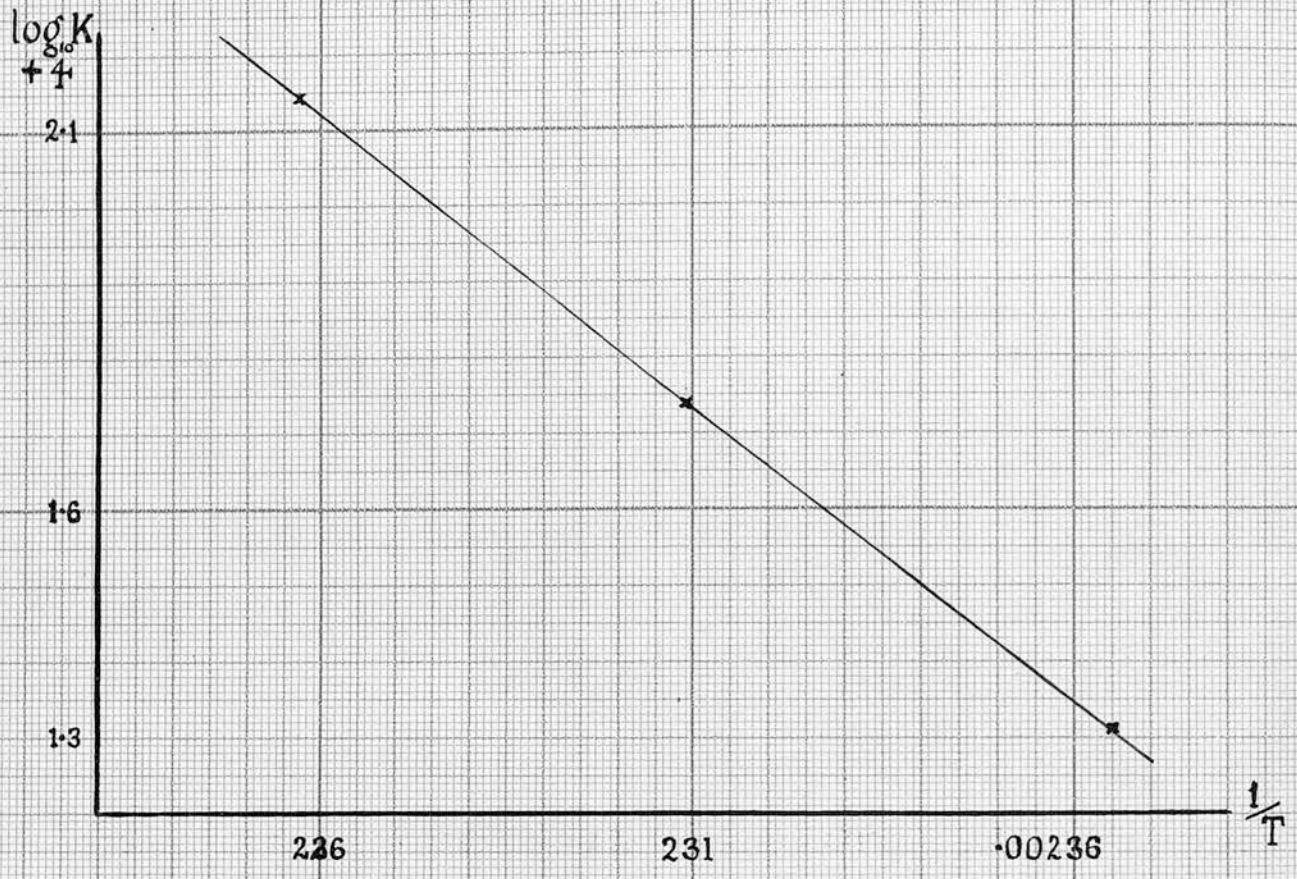
Temperature Coefficient for Oxalpropionic ester.

(see Graph V)

Expt.	T° abs.	K x 10^4	$^1/_T$	$\log_{10}K + 4$
LXXXI	423	31.6		
LVII	"	29.4		
Av.	"	30.5	.002364	1.484
LXXVII	428	51.3		
LIII	"	47.2		
Av.	"	49.2	2336	1.692
LXXIX	433	82.0		
LVII	"	78.5		
Av.	"	80.2	2310	1.904
LXXXII	438	123.1		
LXXXV	"	115.6		
Av.	"	119.3	2283	2.077

(Experiments underlined given in tables 17 to 20)

GRAPH VI: OXALSUCCINIC ESTER.



GRAPH VII: PHENYL-OXALACETIC ESTER.

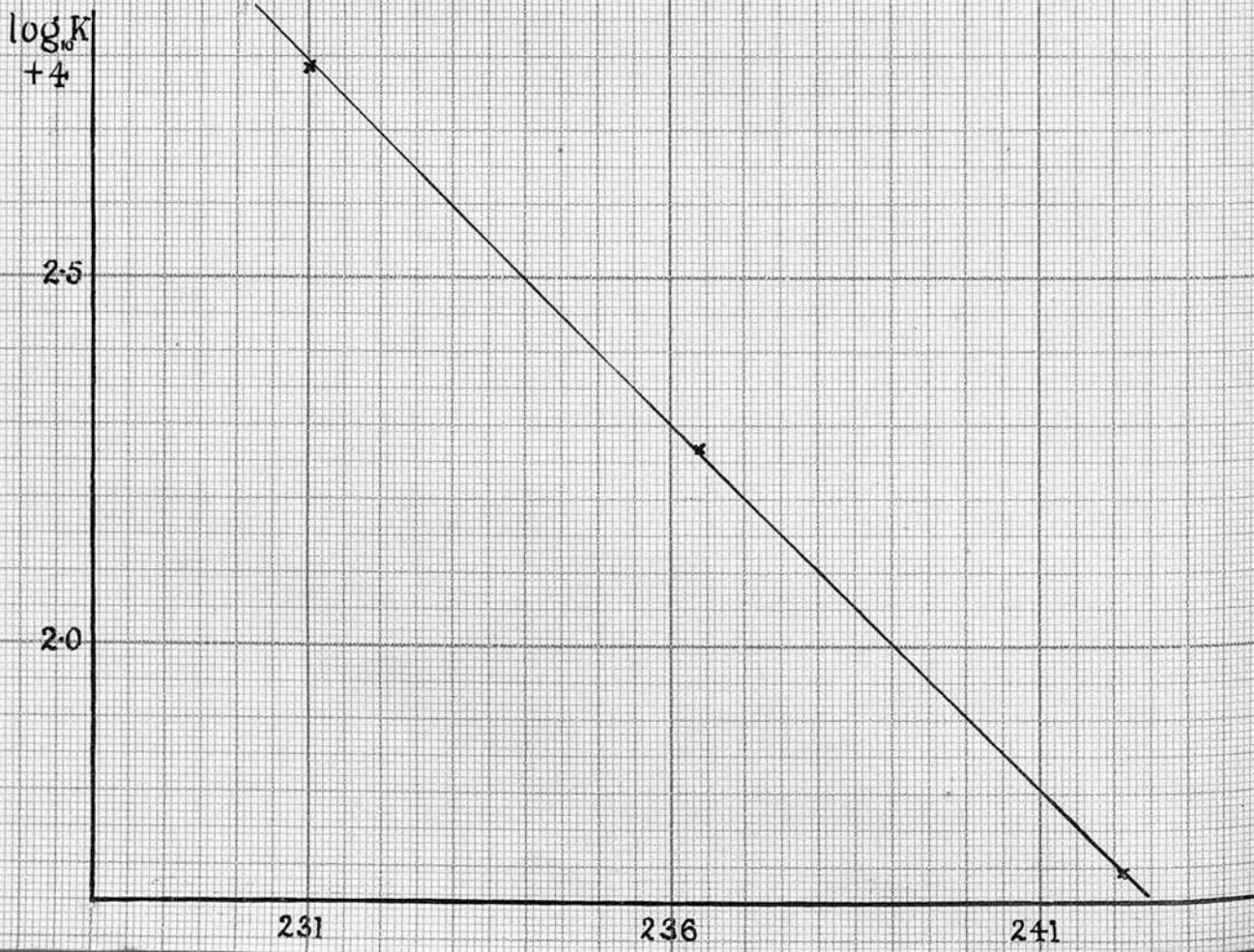


TABLE 25.

Temperature coefficient for Oxalsuccinic ester
(see Graph VI)

Expt.	T^{o} abs.	K x 10^4	$1/T$	$\log_{10}K + 4$
XC	423	18.09		
XCVIII	"	22.83		
Av.	"	20.46	.002365	1.3009
XCI	433	57.3		
XCV	"	56.7		
XCIV	"	50.0		
Av.	"	54.7	2309	1.738
XCVI	443	140.1		
XCVII	"	137.1		
Av.	"	138.6	2257	2.1418

(Experiments underlined given in tables 22 - 24)

TABLE 29.

Temperature Coefficient for phenyl-oxalacetic ester.
(see Graph VII)

Expt.	T^{o} abs.	K x 10^4	$1/T$	$\log_{10}K + 4$
CVII	413	49.7	.002421	1.696
CVI	423	185.9	2364	2.269
CI	433	609.5	2310	2.785

(Experimental results in tables 26 - 28)

TABLE 31.

Summary of Temperature Coefficients.

(showing heat of activation, active life and "active" wave-length.)

R	Q (cals.)	$B = \log_{10} A$	$1/A$ (secs)	λ ($\mu\mu$)	Q/B
$-OC_2H_5$	35,800	13.94	1.1×10^{-14}	795	257
$-CH_3$	33,300	13.36	4.4×10^{-14}	854	249
$-CH_2COOC_2H_5$	35,400	14,30	0.5×10^{-14}	802	247
$-C_6H_5$	44,300	19.88	10^{-20}	641	223

EXPERIMENTS ON THE RADIATION THEORY.

We are now in a position to calculate, by means of the Lewis-Perrin theory, the wave-length of the light, which should be effective in bringing about the decomposition of oxalacetic ester derivatives. Using the relation: $Q\,J = N h\nu = N h\, C/\lambda$

Where N = Avogadro's number = 6.06×10^{23},

h = Planck's constant = 6.55×10^{-27},

C = Velocity of light = 3×10^{10} cm/sec.,

J = 4.18×10^{7} ergs per calorie.

We obtain the values for λ, the active wave-length, given in table 31. pg 78.

	Q	λ
Ethoxy oxalacetic ester	35,800 cals.	795 $\mu\mu$
Methyl " "	33,300	854
Oxal succinic "	35,400	802

Absorption Spectra.

If the theory be true, these substances should exhibit an absorption band in the region near 800$\mu\mu$. This wave length lies just at the edge of the infra-red, a region which, unfortunately, is not easily investigated. There are, however, good reasons for examining the absorption spectra in the visible and ultra-violet. In the first place, modifications of the/

the original form of the radiation hypothesis (Lewis, Trans. Farad. Soc. XVII, Pt.3, 585) suggest that multiples or submultiples of the calculated frequency, may be effective in causing reaction. Secondly, the work of Baly (B.A. Report 1922, p. 294) shows that an absorption band in the near ultraviolet has a frequency which is an integral multiple of the "fundamental molecular" frequency, in the near infra-red.

The spectrograph used was made by Hilger. The first photographs were made with a layer of the ethoxy- and methyl- derivatives in the path of the light from a carbon arc, and are shown in plates I and II. The liquid was contained in a silica cell, whose parallel sides were about 1 mm. apart. It will be seen that there is strong absorption in the ultraviolet, and that this is identical in the two cases.

By comparison with the mercury spectrum, it was estimated that the edge of the band lay between 370 and 390 $\mu\mu$. All light of shorter wave-length (to about 230 $\mu\mu$) was absorbed. The spectrum of the C arc is given for comparison.

Plate III shows the corresponding results with oxalacetic and oxalsuccinic esters respectively. Here the esters were simply held by surface tension between two silica plates, so that the absorbing layer was much thinner. In addition, the spark spectra of magnesium and zinc are given alongside. The edge of the/

PLATE I.

Ethoxyoxalacetic ester with C arc.

PLATE II.

Methyl oxalacetic ester with C arc.

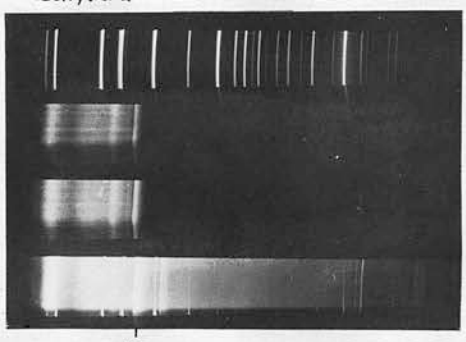


PLATE III.

Oxalacetic (1) and Oxalsuccinic (2) esters with C arc.

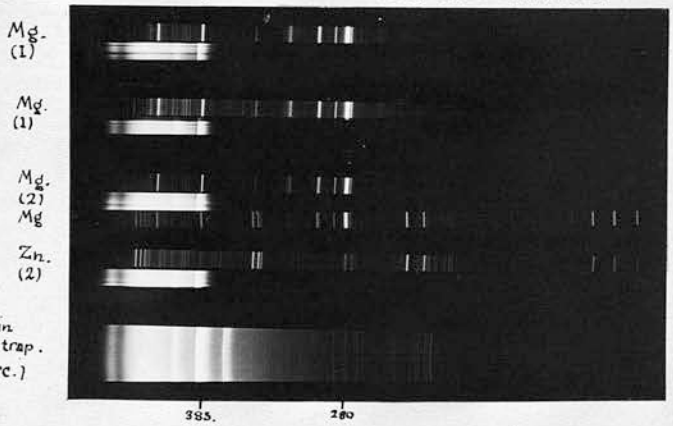


PLATE IV.

0·005 N. Methyl oxalacetic in abs. alcohol

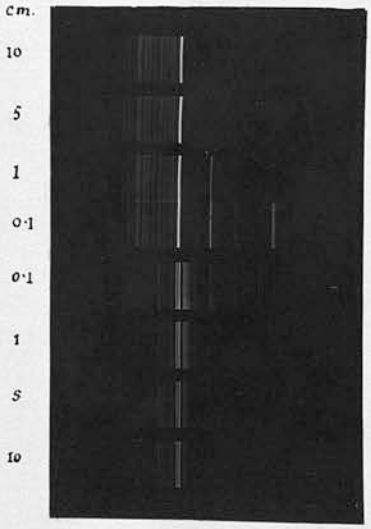


PLATE V.

0·002 N. Methyloxalacetic in absolute alcohol.
Mercury arc.

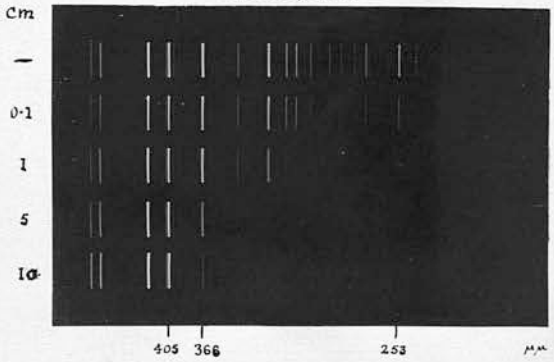
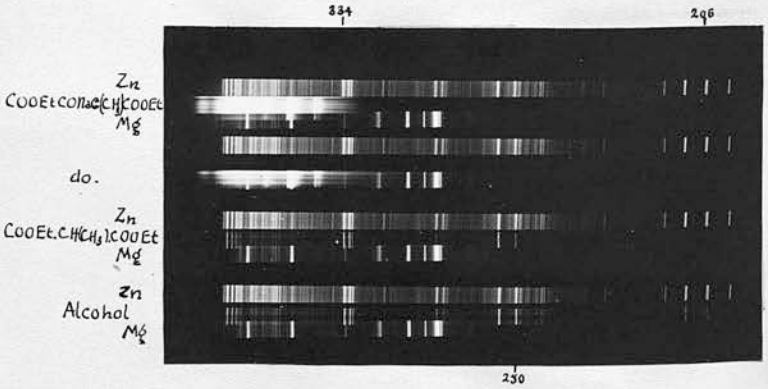


PLATE VI.



the band in this case is less distinct, than before, and slightly nearer the short-wave end of the spectrum. The strong Mg. line, close to the edge, is 383-4 $\mu\mu$ so that we can now say, definitely, that the absorption starts at 380 $\mu\mu$.

This wave-length bears no simple relation to those calculated from the heat of activation. We ought, however, to consider the wave-length of the centre of the band. With a view to determining this, the spectrum of a dilute solution of methyl-oxalacetic ester was photographed in layers of diminishing thickness, by means of a "Baly" tube. It was found convenient to use a 0.005 N. solution of the substance, in absolute alcohol - which solvent is completely transparent in the ultraviolet (see plate VI). In plate IV are shown the results when layers of 10, 5, 1 and 0.1 cm. were used with two different sparks. In plate V, the quartz-mercury lamp was used as a source of light - and the solution was twice as dilute as before. The photographs give no indication of a banded structure; the edge of the absorption simply retreats into the ultra-violet with diminishing thickness of layer.

The photographs of plate VI show the absorption spectra of methyl-malonic ester and of the sodium salt of methyl-oxalacetic ester, which, we can assume, will act like the enolic ester ($COOEt.C(OH)=C(CH_3).COOEt$). The/

The former transmits up to about 250 $\mu\mu$ while the latter starts to absorb about 330 $\mu\mu$. Thus the region from 250 - 330 $\mu\mu$, in the photographs of II, is probably absorbed by the enol-form of the ester, which, as will be shown, takes part in the decomposition. The centre of this region, (290 $\mu\mu$), again bears no simple relation to the calculated frequency. The band from 330 - 380 $\mu\mu$ must be due to the keto-ester.

The spectrum of the phenyl derivative was not examined but the calculated frequency lies in the visible, while the distilled ester is colourless. If there is an absorption band at 641 $\mu\mu$ then, it is very narrow.

Effect of illumination.

As mentioned in the introduction, we can test the Lewis-Perrin hypothesis by exposing the substances to light, of the calculated frequencies. In the event of this proving unable to cause the reaction, it might be conjectured that ultraviolet light in the region of strong absorption, will be effective.

The ester was placed in the "bubbler" (shown as part of the apparatus in diagram 9, pg 85) of clear fused silica, which is transparent to both regions in question. The tube was connected, on one side, to a carbon dioxide Kipp and on the other to a nitrometer, as/

as usual. For illumination, a powerful carbon-arc was used, at a distance of 3 inches. This gives a good continuous spectrum but also radiates a great deal of heat, which was trapped by the cylindrical cell, shown in diagram 9 . The plane ends of this were of clear silica and it carried a steady stream of cold water (Water transmits at the U.V. end as far as silica - see plate III, and down to about 1500 $\mu\mu$ at the other ; silica, of course, is very transparent on both sides of the visible).

Illumination in this apparatus for several hours, of oxalacetic ester and its ethoxy and methyl derivatives produced no recognisable amount of carbon monoxide. In case this negative result were due to an "induction" period, the methyl compound, in one case, was heated till it gave carbon monoxide, shortly before illuminating. Again, the effect of interposing two screens in turn, was tried. The first consisted of a glass cell containing a saturated solution of iodine in carbon disulphide, which would cut out all visible and ultraviolet light. The second was a piece of "U-viol" glass, which transmits from about 328 to 383 $\mu\mu$.* In no case was any decomposition observed. Other experiments in a glass tube, exposing to sunlight and the mercury lamp, and using oxalsuccinic ester were equally unsuccessful.

* Exactly the region already attributed to the keto-ester.

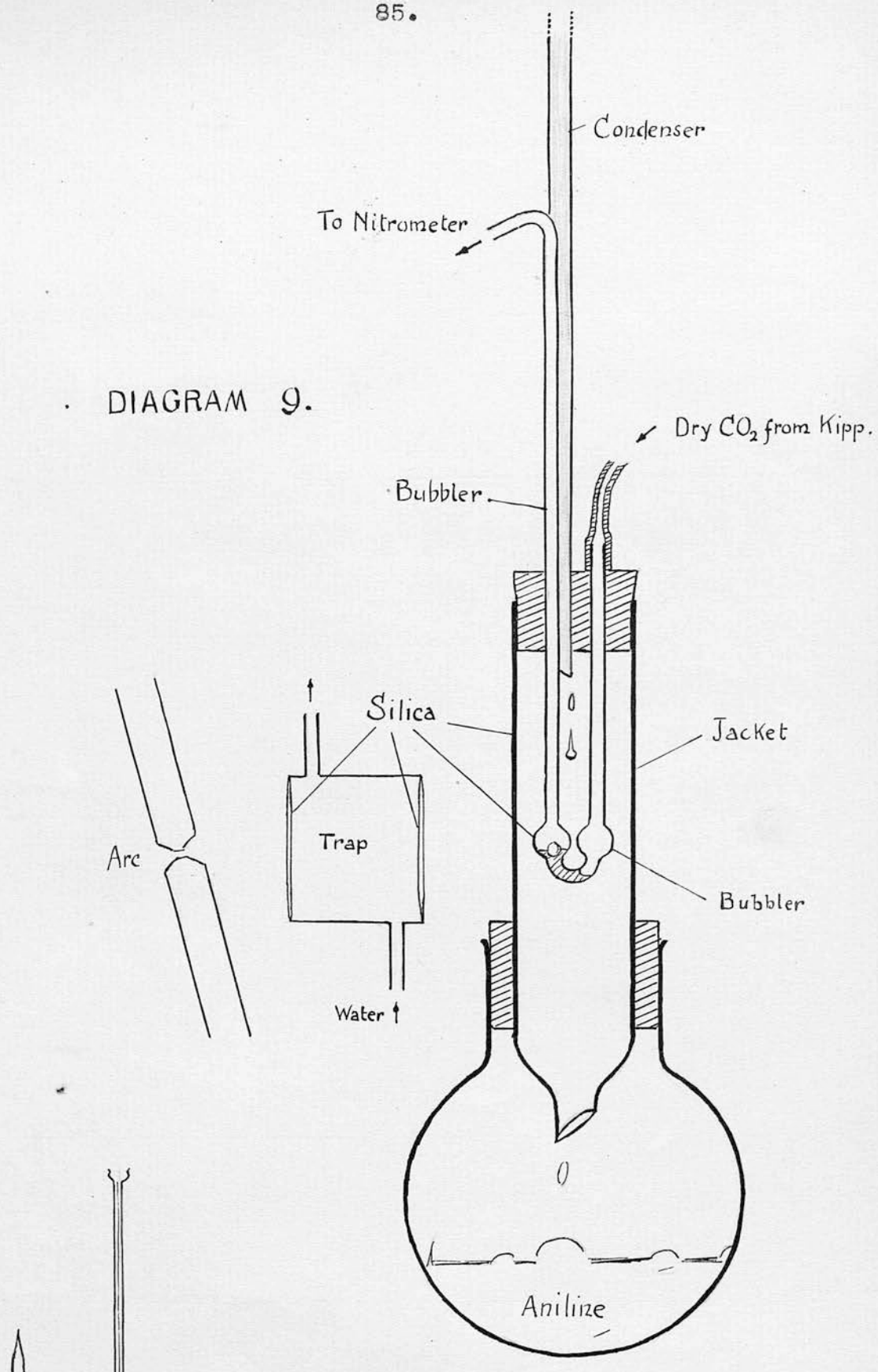


DIAGRAM 9.

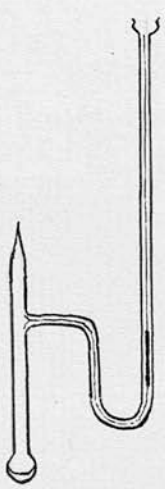


DIAGRAM 10.

However, a little ethoxy ester in a glass tube of the type shown in diagram 10, seemed to give off a gas slowly in the course of several weeks. This cannot be due to thermal decomposition for at room temperature 1 gm. would give 0.00002 cc. in one month.

A more searching test of the influence of light was made by strongly illuminating ethoxy oxalacetic ester at a temperature, at which it decomposes thermally and measuring, meanwhile, the velocity. An acceleration would be anticipated under these conditions. The substance was again placed in the silica bubbler, which was then fixed into the apparatus shown in diagram 9 . The jacket, surrounding the bubbler, was also of clear silica and was kept at 183.8°C by the vapour of the boiling aniline, from the flask beneath. The aniline condensed in the long tube above, which passed, along with the bubbler, through the three-holed cork. A preliminary photograph showed that aniline vapour transmitted up to 320 $\mu\mu$, so that both ultra-violet and near infra-red radiation were available from the carbon-arc source used. As before, the cold-water filter was interposed.

After one or two inconclusive experiments, it was shown that the 'normal' thermal reaction proceeds sensibly unaltered in this apparatus, the value of k at 183.8°C being $\underline{120.5 \times 10^{-4}}$, (See table 32), as against the average value 139×10^{-4} for the numerous/

TABLE 32.

Expt. LXXXIV : Ethoxy-oxalacetic ester at 183.8°C in silica; illuminated by carbon arc.

a = 18.3 cc ; log a = 1.2625 ; t_o = 11 h. 53 m.

t_1	v	c	x	18.3-x	log $^a/_{a-x}$	t	K x 10^4
11.51	start	-	-	-	-	-	-
.55	1.3	0.3	1.0	17.3	0.0245	2	122.5
12.0	3.9	.6	3.3	15.0	.0864	7	123.4
.4	5.5	.7	4.8	13.5	.1322	11	120.2
.9	7.4	.9	6.5	11.8	.1906	16	119.0
.14	9.0	1.0	8.0	10.3	.250	21	119.0
.20	10.8	1.15	9.65	8.65	.325	27	120.3
.30	13.0	1.3	11.7	6.6	.443	37	120.0
.41	14.9	1.5	13.4	4.9	.572	48	119.3
.59	16.7	1.6	15.1	3.2	.757	66	(114.7)
∞	20.1	1.8	18.3				

Average : $k = 120.5 \times 10^{-4}$

numerous 'dark' experiments at 183.5°C. A comparative experiment in the dark, in the same apparatus, gave 122×10^{-4} at 184.3°C. It was also found that the 'slow' reaction (see p. 34.) was unaffected by light. In these experiments, the rather peculiar fact was noticed that the colour of the ester becomes deep yellow, at the instant when decomposition starts.

DISCUSSION OF RESULTS:

The "kohlenoxydspaltung" is shown by oxalacetic ester and all of its derivatives, where one hydrogen of the methylene group is substituted:

i.e. COOEt. CO. CHR. COOEt.

If both hydrogens be replaced - as in dimethyl oxalacetic ester - carbon monoxide is not obtained on heating:

$$COOEt.CO.C(CH_3)_2.COOEt.$$

Except in the case of oxalacetic ester, the reaction seems to proceed nearly quantitatively, though in the experiments described, the yield of carbon monoxide was never more than 95% of the theoretical volume. In the case of ethoxy oxalacetic ester, there is ground for assuming a side-reaction but with the others, no evidence could be obtained of the presence of anything but/

but the malonic ester derivative, in the residue after decomposition.

Quite a number of compounds are known to give carbon monoxide, on heating. For instance, besides formic and oxalic acids, compounds of the type C_6H_5.CO.COOH lose their carbon monoxide in this way. Again dioxo-succinic ester, COOEt.CO.CO.COOEt and mesoxalic ester, COOEt.CO.COOEt behave in the same way. Their similarity in structure to oxalacetic ester is obvious. More closely related to the latter substance are the numerous ortho-diketones, which give carbon monoxide, among other things, on heating. E.g. Acetophenone oxalic ester, $COOEt.CO.CH_2.CO.C_6H_5$, and ketipinic ester, $COOEt.CH_2.CO.CO.CH_2.COOEt$. In fact the group $-CO.CO.\underset{|}{C}H.CO-$ seems to be specially effective in this connection.

It is not necessary that this group should occur in an ester, for the carbon monoxide decomposition may be shown by other types:- For instance: Oxalyl diacetone, $CH_3.CO.CH_2.CO.CO.CH_2.CO.CH_3$ and acetophenone oxalic acid, $COOH.CO.CH_2.CO\ C_6H_5$. With many of the latter compounds, it should be remembered that the loss of carbon monoxide is a side-reaction, the main process at the temperature required, being a condensation.

Mechanism/

Mechanism of the Reaction.

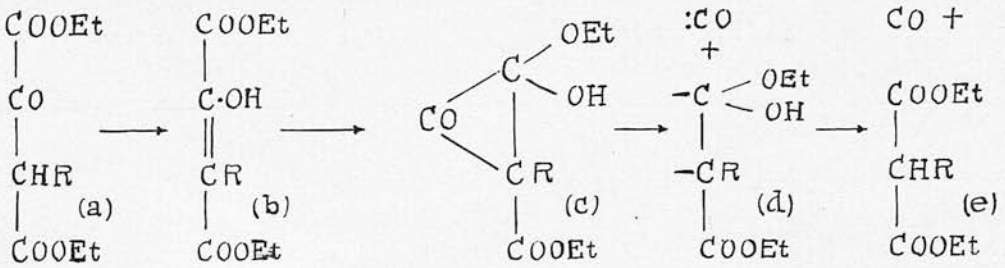
Wislicenus (Ber. XXVIII, 811) showed that the carbon monoxide, which was lost, probably came from the ketonic group and not from the carbethoxy group. Now if this be the case, it becomes a matter of some difficulty, to explain how the CO group can jump out of the middle of the chain, leaving the rest of the molecule intact, unless a linkage exists between the C atoms on either side, just before dissociation. If this is not the case, we must assume that the primary dissociation of the molecule is into three parts, i.e.

COOEt.CO.CHR.COOEt = —COOEt + :CO + —CHR.COOEt

The first and third groups would unite to give the malonic ester derivative, but there is also a possibility that the compounds, COOEt.COOEt (diethyl oxalate) and CHR.COOEt (di-R succinic ester) would be formed.

With this idea in view, the residue after decomposing methyl-oxalacetic ester was examined for a high-boiling succinic ester derivative but without success.

It seems probable then, that the above equation does not hold and, in pursuance of the first hypothesis, the following structural mechanism of the reaction is suggested:



The fact that (b) does take part in the reaction, is confirmed by the failure of dimethyl-oxalacetic ester to give carbon monoxide. This substance cannot exist in the enol-form (b).

It might be argued that we are really measuring the rate of change from (b) to (c), for such isomeric changes often take place with measurable velocity. This is rendered improbable by the fact, that such changes are generally enormously influenced by the nature of the solvent. For instance, Dimroth found that the isomeric change of the triazole derivative proceeded eight times faster, in methyl alcohol than in ether, at the same temperature. (Ann. der Chem. 335, 1). Tubandt's work on the inversion of menthone, (do. 354, 259,) and Lowry's on nitrocamphor (J.C.S., 93, 107) show the same thing. It therefore seems unlikely that this isomeric change is responsible for the measured velocity.

The unimolecular decomposition of the parent compound, oxalacetic ester, which shows so much side-reaction is an interesting side-light on the mechanism of/

of the reaction, but without knowledge of the constitution of the condensation product, we cannot draw any conclusion as to the nature of the second reaction. We have already mentioned that it probably consists primarily of the formation of water.

ABSENCE OF SOLVENT OR IONIC CATALYSIS.

From the results of the experiments on the influence of solvents, it would appear that there is some truth in the statement that, in a unimolecular process, each molecule dissociates without reference to its neighbours. It is true that the velocity is slightly greater in every case, where a solvent is used, but this increase cannot be compared with what is normally known as 'solvent catalysis'. For instance in Menschutkin's classical experiments (Zeit. f. Phys. Chem. 1, 611), we find the velocity in benzyl alcohol is 740 times greater than in hexane.

Two reactions, found in the literature, resemble our present case closely, for both lead to the evolution of a gas from a liquid, and both are truly unimolecular. These are the decomposition of hydrogen peroxide (Bohnson; J. Phys. Chem. 24, 677) and of camphor-carboxylic acid (Bredig and Balcom; Ber. 41, 740). On both of them, however, the solvent has a very/

very marked influence - the velocity varying as much as ten-fold as we pass from solvent to solvent. We may conclude then, that the kinetics of the 'kohlenoxyd-spaltung' are different. Our reaction is more truly unimolecular.

The indifference of the change to acids is perhaps, easier to understand, for the esters (being β ketonic) are very strongly acid themselves, and may, even in the pure state, contain a fair proportion of $H^{\cdot}$ ion. The molecular weights of the ethoxy and methyl derivatives were measured in acetone solution by the boiling point method and found to be normal.

(Ethoxy 213 instead of 232
Methyl 192 " " 202)

so that in this solvent, at any rate, there is little dissociation.

The fact that hydrochloric acid gas and sulphur dioxide do not affect the reaction, is of importance if we are to explain the activation process in chemical reactions by assuming violent collisions; for J.J. Thomson (Phil. Mag. 47, (278) 337) has shown that strongly polar molecules, of this type, should increase reaction velocity by increasing the electrostatic attraction between molecules and hence leading to formation of 'intermediate compounds.'

It is disconcerting to find that drying has no influence/

influence on the dissociation - as far as these experiments show. We cannot conclude, from this, that water is not a catalyst of the reaction, for in cases where the removal of water has inhibited a dissociation, (calomel, NH_4Cl) the extent of the drying was probably much greater than here. Nor can we deduce that Lowry's contention (p. 3) is wrong, when we find that addition of water or $H^{\cdot}$, in comparatively large amounts, does not increase the velocity; for Herzfeld has shown (Zeit. f. Phys. Chem. 1921, 98, 161) that, where two catalysts take part in a reaction, the velocity will generally be independent, of the concentration of one of these. Thus, when a molecule, AB, dissociates with the assistance of the two catalysts, X and Y, according to the equations:

(1) $AB + X \longrightarrow AX + B$; (2) $AX + Y \longrightarrow AY + X$;

(3) $AY \longrightarrow A + Y$

then if reaction (2) is faster than reaction (1) the velocity will be independent of [Y] - the concentration of the second catalyst - provided [Y] is greater than a certain small limiting concentration. If then Y in this case be the water or $H^{\cdot}$, there need be no difficulty in explaining these results.

ANTICATALYSIS BY CARBON MONOXIDE.

While we are discussing the subject of catalytic action, we have to account for the retardation in velocity,/

velocity, first observed when the stream of carbon dioxide was interrupted between readings (p. 34). Three suggestions have already been advanced to explain this effect. The first - that the retardation is due to reduction of the exposed surface - is disposed of by expt. LXXXVIII (p. 43), while the hypothesis of reversibility - improbable a priori - has been found by direct trial to be unfounded. It is proposed to show that these results and also the retardation in the absence of a stream of gas, can be explained on the theory that, at fairly large concentrations, the velocity is inversely proportional to the concentration of carbon monoxide: i.e. that the carbon monoxide is an "anticatalyst."

In the first place, we have to explain the fact, that the dissociation, though retarded so much, when no stream of carbon dioxide is used, still follows very accurately, the unimolecular law, as in Table 12. We must remember, that at any instant, the effective concentration of carbon monoxide will not be determined by the time. For, once the gas has started to leave the liquid under its own pressure, its concentration will remain at a steady value, determined by its solubility in the liquid; and, though the composition of this liquid is constantly changing, the chemical nature of the solvent-molecule does not alter very much. Thus its solvent action may well change little as/

as the experiment proceeds, and the concentration of the anticatalyst will remain constant:

$$\frac{dx}{dt} = \frac{k(a-x)}{[CO]} = \frac{k(a-x)}{\text{Constant.}}$$

i.e. unimolecular.

It is evident that this explaination can be extended, to explain why a unimolecular constant should be obtained with the ethoxy derivative, when an intermittent stream of carbon dioxide is used. During the short time that the stream is actually passing, the reaction will presumably proceed with the true velocity. When the stream is stopped, however, the carbon monoxide will quickly reach a saturation value. From this point, the conditions are the same as in the previous case.

In conformity with this, the retarded velocity by both methods, for the ethoxy derivative, is about one-half the true velocity.

That this explanation will not apply to the methyl compound is shown by expt. LXXXVI, table II, where instead of a unimolecular decomposition, we find the instantaneous velocity remains constant throughout the experiment. This result means, that according to our hypothesis:

$$\frac{dx}{dt} = \frac{\text{Conc. (oxalpropionic)}}{\text{Conc. (CO)}} = \text{constant.}$$

Hence/

Hence the concentration of carbon monoxide in the liquid must diminish at the same speed as the reacting substance. This may happen for several different reasons; it is sufficient to assume that the gas is much less soluble in the ester-mixture.

As regards the reason, for this function of the carbon monoxide, it is possible to make a guess. Whatever view we take of atomic and molecular structure, it is certain that the freshly-liberated carbon monoxide, besides containing a great excess of energy, will be so arranged as to leave two free positive valencies (=C=O or $\rightarrow \dot{\underset{\cdot\cdot}{C}}:\dot{\underset{\cdot\cdot}{O}}: \; \leftarrow$)

However rapidly this changes to the stable form, the fields of force due to these valencies will have the power to influence the configuration of neighbouring molecules, even though no intermediate compound be formed. It is to such an action as this, that Bjerrum (Zeit. f. Phys. Chem. 108, 82,) has recently given the suggestive name of "deformation catalysis."

It only remains to explain, why the temperature coefficient of the 'slow' reaction should be nearly twice that of the normal

i.e. Intermittent CO_2: Q = 55,600 cals.(Ethoxy.)

No CO_2 : Q = 61,200 cals.(Methyl.)

If our assumption is right, this means that, in both cases, the oxalacetic molecule must absorb very much/

much more energy if it is to dissociate,in the face of resistance by the carbon monoxide molecules. Such high values of Q are often found in heterogenous reactions. A little reflection will show, that we are probably not measuring a homogenous reaction-velocity here,for the oxalacetic ester has to produce, by dissociation, carbon monoxide with sufficient energy to leave the surface of the liquid.

RADIATION EXPERIMENTS.

The belief in the intervention of radiation in all Chemical changes receives its most direct support from the number of reactions, which proceed in the dark but which can be very much accelerated by light. (Cf. For instance Dhar: Trans. Farad. Soc. XVII (3) 601). In contrast to those, many reactions are brought about under the influence of light (of a definite region of the spectrum) but do not occur in the dark. Among the latter, the dissociation of organic compounds to give carbon monoxide is fairly common. Thus phosgene, formamide, acetone, fenchone and diethyl ketone easily split off carbon monoxide when illuminated under certain conditions.

Eg. $CH_3.CO.CH_3 = CO + CH_3CH_3$

Thus we have some grounds for expecting a ketone, such/

such as oxalpropionic ester, to dissociate photochemically. This expectation is very much enhanced, by the fact that orthodiketones have recently, been shown to give carbon monoxide, when illuminated by ultraviolet light (J. Amer. C.S. 45, 1827). Benzil vapour gives benzophenone, while diacetyl vapour gives ethane in this way.

None of the compounds examined, however, show definite evidence of decomposing as a result of illumination alone. The existence of an induction period has already been put forward as a reason for the absence of photochemical action. Noyes and Kouperman found that the photochemical decomposition of oxalic acid itself, by ultraviolet light, was preceded by a long induction period. (J. Amer. C.S. 45, 1398). That this is the real explanation, is rendered improbable by the result of expt. LXXXIV (table 32.), where the substance was actually decomposing, when exposed to the light.

The failure of these experiments is of importance, from two distinct standpoints. We know, from the absorption spectra, that these derivatives of oxalacetic ester absorb light strongly, over a wide region in the ultraviolet; yet the excess energy, acquired in this way, does not seem able to stimulate dissociation. Now, according to Baly, such a band is characteristic of the change between two quantum states or/

or phases of the molecule; by exposing a substance to light which it absorbs, we convert it into a "more reactive phase" - an idea, which our experiments do not confirm. There is some reason then, for thinking that this absorption is due to the change, "keto" $\rightleftharpoons$ "enol", as has been supposed by Hantzsch and others.

In the second place, they show that the Lewis-Perrin hypothesis, in its simple form, does not apply. This result is in agreement with all other cases, where the theory has been subject to direct test - with perhaps, one exception. (Triethyl sulphine bromide has been found to show an absorption band at the frequency calculated from its velocity temperature-coefficient).

It does not follow from this, however, that radiation cannot play a part in every reaction. Two conceptions suggest themselves as to why the crude relation of Perrin and Lewis does not fit the facts.
(a) Assuming the truth of the Einstein photochemical law, the quantum, necessary to decompose the molecule, may be characteristic of the energy of one of the internal modes of motion and not of the total critical energy. (See Langmuir J. Amer. C.S. 42, 2190).
(b) Most "unimolecular" reactions of measurable speed, probably take place in two stages, with the assistance of a catalyst. We can represent the uncatalysed reaction by

AB/

$$AB \longrightarrow A + B \qquad (1)$$

and, where X is the catalyst, by

$$\begin{cases} AB + X \longrightarrow AX + B & (2) \\ AX \longrightarrow A + X & (3) \end{cases}$$

Let the heats of activation be respectively Q , q_1 and q_2. Now if (1) is immeasurably slow, unless when X is added, then Q must be considerably greater than q_1 or q_2. It does not follow, as J.J. Thomson assumed, that $q_1 + q_2 = Q$.
If q_2 is greater than q_1 , then reaction (3) will determine the speed of the process and our measurement of temperature coefficient will give us the value of q_2. Now, if the catalyst is ineffective in the photo-chemical dissociation of AB , the necessary quantum will be determined by $Q = Nh\nu$. As there is no necessary relation between Q and q_2 , we can see why the method of Lewis is unsuccessful in predicting the active frequency. It is important to note here that with the given condition, $q_2 > q_1$, the reaction will remain a unimolecular process.

HEAT OF ACTIVATION AND LIFE OF AN ACTIVE MOLECULE.

The graphical method of examining the results, shows that ethoxy-and phenyl-oxalacetic, oxal-propionic and oxalsuccinic esters decompose in conformity with the/

the Arrhenius law. This in itself, is of little importance for, in nearly all homogeneous chemical reactions, the law holds good. The values of Q and A in the equation $k = A_e^{-Q/RT}$, however, are of great interest. We find that, with one exception, Q lies between 33,000 and 36,000 calories and B (= $\log_{10}A$) is about 13 to 14. An examination of the available data shows that Q and B, for other unimolecular reactions, generally lie close to these numbers and we are, therefore, justified in concluding that we have been actually measuring the velocity of a chemical change, not of some accompanying physical process (such as diffusion).

It is a remarkable fact that the value of Q, for practically all unimolecular reactions, lies so close to 30,000 calories - as will be seen on referring to the tables prepared by Christiansen and Kramers and by von Halban (Zeit. f. Phys. Chem. 104, 470 and 67, 174). The agreement still holds when we are dealing with those pseudo-unimolecular reactions, in which the solvent plays a part. Even the one authentic unimolecular gas-reaction has a value of Q not far removed from 30,000 (= 24,800 cals.)

Now, there is no doubt that Q is the amount of energy which must be acquired, in some way, by the molecule, before it will react; but we must remember, that the range of velocities, which we can detect or measure/

measure in a laboratory, is comparatively small. On the one hand, we cannot directly estimate velocities, where the half period is less than 2-3 seconds and on the other, those whose half-period is longer than 10 - 20 days. Thus the constancy of Q is possibly an outcome of the fact, that we only deal with molecules, whose stability lies within well defined limits. An explanation similar to this was first introduced by Bodenstein, to explain the "R.G.T. rule" for all Chemical reactions.

In this connection, an observation due to von Halban is also of interest - namely, that unimolecular reaction-velocities are much more dependent on change of temperature, than those of higher order. Expressed otherwise, this means that we must give more energy to a single molecule, than to a molecular complex, to cause chemical reaction. It is therefore of some importance to find that the values of Q in the "kohlenoxydspaltung" are very high, even for a unimolecular reaction. Only in three of the reactions mentioned in the above tables, does Q reach so near to 36,000 calories. (N.B. In von Halban's table: $Q = 2.3\ R\ "A" = 4.6\ "A"$). As regards the value of 44,300 cals., for the phenyl compound, no authentic homogeneous reaction has yet shown such a large heat of activation.

The values of B , the integration constant, generally/

generally show a similar consistency and our reaction is very close to the average with 13 or 14 (again ignoring the phenyl derivative). In table 31 the value of $\frac{1}{A}$, the average life of an active molecule (see Part II) has been calculated in each case (where $B = \log_{10} A$). The value of 10^{-13} - 10^{-14} secs will be shown, in part II of this thesis, to be in agreement with the conception of activation by collision.

The variation in the values of Q and B, due to the change of the substituent group R, shows at once one regularity: the values of the two constants vary in a roughly proportional manner - Q increasing, when B increases, and similarly for a decrease, 'mutatis mutandis'. This is seen more clearly from the values of Q/B (given in the table 31), which are roughly constant. The only results available, for comparison, are those of Nicoll and Cain (J.C.S. 83, 470) for the velocity of the change.

$R - C_6H_4.N_2.Cl + H_2O \longrightarrow R.C_6H_4.OH + N_2 + HCl$,

where the group R was subject to variation.
The values of Q and B (borrowed from Christiansen and Kramer's table) are given below, together with Q/B.

R	Q	B	Q/B
- H.	24,300	13.6	1790
o-CH_3	25,100	14.6	1720
m-CH_3	22,900	13.0	1760
p-CH_3	27,900	15.0	1860
p-SO_3H	28,200	14.9	1890
(m-NO_2	30,500	15.0	2030)

Though, strictly speaking, this is a bimolecular reaction it is obvious that the relation again is valid. This point, so far as the writer knows, has never before been noticed.

Exactly the same parallelism between Q and B is found, when the variations are produced, not by changing the molecule, but by using different solvents, with the same substance. This is shown by the results of von Halban on the dissociation of a quaternary ammonium bromide in chloroform, bromoform and tetrachlorethane (Ber. 41, 2417) and on the dissociation of triethyl sulphine bromide in six different solvents. (Cf. Also Fawsitt and Burrows; J.C.S. 105, 609. and Lueck; J. Amer. C.S. 44, 757). The phenomenon throws an interesting light on the nature of solvent catalysis, for, actually, the solvent seems able to affect the stability of the molecule in exactly the same way as the substitution of a new group. There is thus reason for assuming, that the solvent can distort the molecule/

molecule just as the introduction of a group of large molecular volume would.

The fact, that the active life of the molecule varies inversely as the heat of activation is in accordance with the ideas of Bohr, in the region of atomic structure. An atom in an "energy-rich" state has a much smaller chance of survival, than one, which is near the normal. Thus, the meaning given by Christiansen and Kramers to A in the equation $K = A\ e^{-Q/RT}$ receives indirect confirmation, from this fact. It may be pointed out, in passing, that we have here, a clue to the partial success of the equation of Dushman, who took $A = \nu$, where $Q = Nh\nu$, or in other words Q/A = constant (Nh). (See Part II, p. 119)

LIQUID REACTIONS.

It will be noticed, on examining the known unimolecular reactions in the liquid state, that a solvent is usually employed - generally, in fact, in much greater quantity than the reacting substance. Only one case where the pure substance has been used, is known - the decomposition of fused malonic acid (Hinshelwood J.C.S. 117, 156). Here, however, there was some abnormal factor, for the results apparently did not obey the Arrhenius law. The "kohlenoxydspaltung" is therefore a unique reaction, in that it is the only case where/

where a pure liquid dissociates normally according to the unimolecular law.

It has been suggested, that the decomposition of a pure liquid should differ greatly from that of a solution of the same substance, but the results, here, show that suggestion to be unfounded. In fact, it may be questioned whether, really, there is any difference between a unimolecular gas reaction and the same process in solution, for nitrogen pentoxide gives the same values, approximately, of Q and B, whether the reaction occur in the gaseous state or in solution in chloroform.

AUTOCATALYSIS.

The striking and unexpected difference in the behaviour of phenyloxalacetic ester remains to be explained. Positive auto-catalytic unimolecular reactions are not unknown. Kullgreen (Zeit. f. Phys. Chem. 41, 407) found that the inversion of aqueous cane sugar, in the absence of acid, followed the equation,

$$\frac{dx}{dt} = k\,x\,(a - x)$$

- the effect being subsequently traced to an acid, formed from the 'invert' sugars. The hydrolysis of methyl acetate, by acetic acid, is of the same type for the acetic acid formed catalyses the reaction. (Ostwald/

(Ostwald, J. pract. Chem. **28**, 449)

It is reasonable to suppose, that the circumstances, which lead to an autocatalytic constant, with the phenyl compound, are latent in the case of the other four derivatives. This view is supported by two considerations: (a) The decomposition of oxalpropionic ester, in every case, shows distinct traces of a lag at the beginning of the experiment, such as we should expect, if the reaction were autocatalytic during this initial period. Thus the times, elapsing between the "start" and t_0, are respectively 13, 8, 13 and 6.5 minutes, whereas it is evident, from the oxalsuccinic results, that 2 minutes is quite sufficient, for the attainment of equilibrium with the bath. (Cf. Expt. XCI, table 23, p.69.) In the former case then, the effective concentration of the methyl malonic ester molecules probably takes a little time to reach a constant value. (b) The experiments with the dilute preparation of the phenyl derivative, show that it is possible to obtain very satisfactory agreement with the unimolecular law, even when the reaction is known to proceed, in fact, otherwise. (tables 26 to 28).

We get an even clearer picture of the possible state of affairs, when we consider the case of Ostwald's reaction (mentioned above). If we use acetic acid, as a catalyst for the hydrolysis of methyl/

methyl acetate, the acid produced gives sufficient $H^{\cdot}$ to influence the velocity and the reaction is autocatalytic. If, on the other hand, we use hydrochloric acid, the influence of the acetic acid formed is negligible and the unimolecular law is followed.

i.e. $\frac{dx}{dt} = k_1 x (a - x)$ becomes $\frac{dx}{dt} = k_2 (a - x)$.

We have already explained how the unimolecular constant, k_2, becomes $= k_1 a$, where k_1 = true autocatalytic constant.

If the energy of activation is acquired by collision, those molecules, in the system, which contain the greatest amount of internal or kinetic energy, will be most effective in activating the reacting molecules. Now the freshly-formed product (in this case the phenylmalonic ester molecule) will be highly energised, because it still contains the heat of activation which was necessary to bring it into the active state. Thus the collisions between the inactive reactants and the active resultants, will be the most fruitful source of active reactants - a conception of unimolecular reaction due to Christiansen and Kramers (loc. cit.). In part II of this thesis, the consequences of this assumption are developed mathematically, and it is predicted - that in such a reaction, where the deactivation of the products is reversible, the reaction will be <u>autocatalytic</u>.

Thus/

Thus the behaviour of phenyl-oxalacetic ester is strong evidence in favour of Christiansen and Kramer's assumption. Their own mathematical deductions, from the same assumption, do not lead to this conclusion but that will be shown to be due to the fact, that they virtually assume simple 'Arrhenius' equilibrium, between active and inactive molecules.

We have supposed, of course, that the phenyl-malonic ester and not the carbon monoxide,is the catalyst, since the latter is continuously removed. We are faced, however, with the difficulty, that one of the products retards the reaction, and the other accelerates it. This can be simplified by assuming, that the primary effect is the positive catalysis by the malonic-ester derivative, and that the smaller, carbon-monoxide molecules merely inhibit this action, by getting in the way - their nascent valencies coming into play, as already suggested. It would seem, then, that the larger molecule carries away a much greater share of the activation energy. A simple explanation of this is given by the principle of equipartition of energy. Just before dissociating, the total internal energy will be equally distributed between the numerous degrees of freedom of the molecule. When the molecule splits, the more complex part-molecule will contain more energy in virtue of its greater number/

number of degrees of freedom (E.g. Phenyl malonic ester has 33 atoms, as compared with 2 in carbon monoxide.)

The exceptionally large heat of activation (44,300 cals) is in agreement with the above hypothesis, for the molecules of the reaction product, which contain this, will show more tendency than with the other derivatives, to hand back their energy to the reactants. The value of the 'active life', ($\frac{1}{A} = 10^{-20}$ secs.) makes it certain that here, there is no equilibrium between active and inactive molecules; for the molecule remains active, on the average, for 10^{-6} of the time, taken by a collision.

The discovery of this autocatalytic change sheds a new light, on the question of unimolecular reaction, for here, at least, we have direct evidence of the rôle played by collisions, in the process. Further, there is nothing in the nature of things, to prevent all known unimolecular reactions from being, as here, autocatalytic reactions in disguise.

PART 2.

THE THEORY OF THE UNIMOLECULAR REACTION.

It has long been realised that it is impossible to account, by a simple application of kinetic theory, for the enormous increase in the velocity of chemical reactions, when the temperature is raised. The observed acceleration, indeed, is a hundred times that calculated from the increase, due to temperature, in the number of collisions. Now, Arrhenius (Zeit. f. Phys. Chem. 4, 226) found, in 1889, that the influence of temperature on the velocity constant could be represented by the equation:

$$\frac{d}{dT}(\log K) = \frac{Q}{RT^2} \qquad (a)$$

- a relation which has since been verified in numerous instances. Arrhenius assumed that two kinds of molecules - "actives" and "passives" - existed in equilibrium and that the former, which would be present in very small concentration, were alone capable of reacting. He was unable, however, to explain rigidly, why the "equilibrium" was displaced so quickly by rise of temperature, as we must infer if equation (a) holds.

In the case of unimolecular reactions we are faced/

faced with another fundamental difficulty. With bi- and tri- molecular processes, we can explain the law of change on the basis of the principle of "mass-action". We assume, for instance, that a molecule A will have a chance, which is proportional to its concentration, [A], of colliding with, and therefore of combining with a molecule B. If A is decomposing unimolecularly, the velocity of change at any instant will again be found proportional to [A] but obviously, we cannot explain this on the same grounds as before, as there seems no reason to suppose that A must collide with another molecule, before it dissociates. To express the difficulty in another way: in a unimolecular reaction the law of change is the same as in a radio-active transformation, namely, that there is a constant probability that a certain molecule will decompose within the next second.

$$k = -\frac{1}{Cn} \cdot \frac{dCn}{dt} \qquad (b)$$

Why does this law lead to the Arrhenius relation just as the law of mass-action with reactions of higher order?

Within the last ten years, numerous solutions have been offered of these two difficulties.

RADIATION/

RADIATION HYPOTHESIS.

Of these, the theory, that all reactions proceed by the absorption of the energy (Q) as radiation of a certain frequency, has attracted most attention. This idea first occurred to Trautz in 1906 and, independently, to Lewis and Perrin in 1913, all of whom developed a quantitative theory. Lewis & Perrin showed that the frequency of the active radiation, for a unimolecular process, would be obtained from the Q of Arrhenius' equation by setting $Q = Nh\nu$, where N is Avagadro's number and h is Planck's constant. A number of direct experiments, since that time, have shown that the theory is probably quite erroneous. It does not seem, however, to have been sufficiently emphasised that the arguments, with which the theory was supported, are open to serious question.

Firstly, no reason, save that of simplicity, is given as to why the active light should be mono-chromatic. Secondly, Lewis (B.A. Rep. 1915, 394) shows on his assumptions, that the Einstein photochemical law must hold for thermal reactions - a fact which he takes as a confirmation of these assumptions. As a matter of fact $Q = Nh\nu$, is contained implicitly in the two hypotheses: (1) that the active radiation is monochromatic. (2) that the Planck law for the radiation from a black body is obeyed.

Perrin's/

Perrin's reasoning (Ann. de Physique II, 6, 1919) is also open to attack. He asserts that dilution and change of pressure have no effect on the velocity constant of a unimolecular gas reaction. The only results available, when he wrote, - those of Trautz & Bhandarkar for phosphine - (Zeit. Anorg. Chem. 1919, 106, 95) have since been shown by Hinshelwood (J.C.S. 125, 393, 1924) to apply to a heterogeneous reaction. Three years ago, Daniels & Johnston (J. Amer. C.S. 43, 53) showed that the thermal decomposition of nitrogen pentoxide is uninfluenced by change of pressure. At the lowest pressure in their experiments, however, there are 10^{18} molecules to the cc., while the changes of pressure employed were of the order 10^{1}. Perrin is therefore begging the question, when he states, that an isolated molecule would behave similarly.

As a matter of fact, the radiation theory of Lewis & Perrin does not mention or explain why all molecules are not able to benefit by the active radiation. For, if so, all the molecules would take an equal time to absorb the necessary quantum and the decomposition would be instantaneous - a suggestion due to Van t'Hoff. The fallacy of such a conclusion, of course, lies in the fact, that no account is taken of the distribution of energy among the molecules, before the radiation is applied.

In point of fact, Perrin himself, almost exposes the/

the main weakness of his argument. He admits that the number of very violent collisions increases sufficiently with temperature, to account for the effect of temperature on reaction velocity - an idea which he dismisses, by saying that such shocks produce ions. This is not true. There is no evidence that purely thermal ionisation has been observed in any of the commoner gases. (Richardson: "Emission of Electricity from hot bodies" 2nd Ed. p.314). Even if ions can be formed by collision, when the molecules are reacting, it is well known that ions are very efficient promoters of chemical reaction.

Probably the foremost critic of the Lewis-Perrin theory is Irving Langmuir (J. Amer. C.S. 42, 2190). His criticism is, that the amount of energy radiated from a black body, in the neighbourhood of the calculated frequency, is utterly inadequate to account for observed velocities of thermal reactions. Unfortunately, however, his calculation is based on the erroneous results of Trautz and Bhandarkar. A similar calculation has therefore been made for the thermal decomposition of ethoxy oxalacetic ester (see Pt. 1) Using Planck's formula for the energy of a particular wave-length in the "hohl-raum" radiation -

$$E_\lambda \, d\lambda = \frac{8\pi c^2 h}{\lambda^5} \cdot \frac{1}{e^{\frac{ch}{\lambda kT}} - 1} \, d\lambda$$

we find, that for a region of 10 $\mu\mu$ near wave-length 800 $\mu\mu$, the energy radiated from 1 sq. cm. of surface at 183° is 2.1×10^{-7} ergs/sec.

The absolute velocity constant at this temp. = $0.014 \times \frac{2.3}{60}$ and hence the energy required in 1 second by 1 cc. (assuming density = 1) (See table 31)

$$= 35,800 \times .014 \times \frac{2.3}{60} \times \frac{1}{232} \times 4.2 \times 10^{7} \text{ ergs}$$

i.e. 3×10^{6} ergs.

The required energy is 10^{13} times that available in the black body radiation from 1 sq. cm. and Langmuir's criticism is therefore valid.

The discrepancy is so marked, that one is led to speculate whether the <u>whole</u> of the thermal radiation would be sufficient to activate the molecule - a suggestion which is the basis of Tolman's theory of unimolecular reactions. Using Stefan's equation

$$E = 5.72 \times 10^{-5} \theta^{4}$$

we find that, at 183°, the total energy radiated from 1 sq. cm. in 1 second is 2.4×10^{6} ergs. Thus if the cc. of ester were enclosed in a cubical box, there would be about five times the necessary amount of energy in the radiation. The dissociation of N_2O_5 at 45° (Expt. 7) gives the following results:

($K = 5 \times 10^{-4}$, $p = 34.8$ cm., $Q = 24,700$ cals.)

Energy required during first second by 1 cc.

$$= 0.9 \times 10^{4} \text{ ergs.}$$

Total radiant energy from 6 sq. cm.: all frequencies

$$= 3.5 \times 10^{6} \text{ ergs./sec.}$$

Hence in this case, there is ample energy for the purpose. It is possible, then, that if the effective region of the spectrum is sufficiently broad and near enough to the wave-length of maximum energy, that some radiation theory may stand examination from this point of view.

Despite the failure of the present radiation theory, it is surely evident that the vibrations of a molecule will be influenced, in some way, by the radiation field. In this connection, we would quote a statement of Jeans[1]: "The molecules and the ether must be regarded as forming a single dynamical system, the two constituent parts of which - the matter and the ether - interchange energy freely with one another through the mechanism of radiation". ("Dynamical Theory of Gases", 2nd Ed. p.223).

It is not, however, necessary to postulate the intervention of radiation in order to dispose of the first dilemma enunciated at the start, for, in 1914, Marcelin (Comptes Rendus 158, 116) showed, by means of the Boltzmann-Gibbs principle, that if a molecule reacts when it has acquired an energy E_C in excess of the normal, then $\frac{d}{dT}(\log K) = \frac{E_C}{RT^2}$ (or $\frac{Q}{RT^2}$)

Arrhenius, indeed, had always regarded the Q of his equation as the "heat of activation", which must be supplied before a molecule becomes active, but only now was this idea and his equation, itself, placed on a sound theoretical basis. E_C, Marcelin /

Marcelin called the "critical increment" but he made no assumptions as to how this energy was acquired. The explanation holds for reactions of any order and thus Marcelin shows us how to account for both our difficulties.

THE SECOND INTEGRATION CONSTANT.

This advance does not exhaust the question, for, though it succeeds in explaining Q, there is another constant of whose meaning we are ignorant. Integrating the above equation we obtain

$$\log_e K = -\frac{Q}{RT} + B \quad \text{i.e. } K = e^{-Q/RT} \times e^{B}$$

$$\text{(c)} \quad \text{or } K = S\, e^{-Q/RT} \text{, where } B = \log_e S.$$

Marcelin's work leaves the integration constant, S , unexplained. This quantity is a frequency, for $\frac{Q}{RT}$ is a pure number while K has the dimension of frequency (= time^{-1}). It was suggested by Dushman, (J. Amer. C.S.) that this frequency might be identical with that obtained by assuming Q to be absorbed in quanta ($Q = Nh\nu$) and the expression for a unimolecular reaction would then become:

$$k = \nu e^{-\frac{h\nu}{kT}} \quad . \qquad \text{(d)}$$

Dushman made no attempt to give a logical explanation/

explanation of this equation and any validity it may have, arises from its agreement with fact. Tolman (J. Amer. C.S. 43, 269) found that Daniel's and Johnston's results were in fairly good agreement with it and the results of the writer show the same thing. (Part 1) Eg:

Methyl oxalacetic ester at 155°: (λ = 856 $\mu\mu$)
k(calculated) = 1.4 x 10^{-3}; k(observed) = 1.9 x 10^{-4}.

Several authors have given an explanation of this formula to account for its partial success. E.g. Rideal. (Phil. Mag. 1920, 40, 461). Rice, McKeown & Lewis. (Phil. Mag. 272, 46, 312 seq.). On the other hand, Langmuir (J. Amer. C.S. 42, 2199) and Christiansen (Zeit. f. Phys. Chem. 103, 91) prefer to write the formula

$$k = \nu_1 \; e^{-\kappa \frac{h\nu}{RT}} \quad \text{Or} = \nu_1 \; e^{-Q/RT}$$

- the supposition of identity of the two frequencies, being rejected.

Two attempts have been made to use a radiation theory in accounting for constant S by Trautz and Tolman (Zeit. Anorg. Chem. 102, 81, 1918 and J. Amer. C.S. 42, 2506). In both cases, however, the physical picture used is so crude and improbable as to justify our ignoring the rather complicated expressions obtained. On the one hand, Trautz supposes that a molecule dissociates when the two constituent parts collide/

collide with each other, while Tolman assumes that the molecule absorbs radiation of all frequencies.

Exact formulae for the velocity of a unimolecular change based on the assumption of activation by collision, have been developed by Herzfeld, (Ann. der Phys. 53, 613), Rodebush (J. Amer. C.S. 45, 606) and J.J. Thomson (Phil. Mag. 1924, 47, 368).

Of all these formulae, the one which gives us the most exact and plausible conception of the unimolecular process is that due to Christiansen, which was later revised and reconsidered by Christiansen & Kramers in 1923 (Zeit. f. Phys. Chem. 104, 451). We are impelled to accept this, as the best treatment up to date, for the reason that the equation is derived by extending the quantitative application of the quantum theory of states, from atomic to molecular phenomena. The starting point is the expression due to Einstein for the number of molecules in mth state $N_m = C\ p_m\ e^{E_m/RT}$ when the distribution is determined by collision, and where p_m is the 'a priori' probability of the mth state and E_m is the energy corresponding.

These authors assume that the number of "active" molecules[(a)] is governed by this relation but, at the same time, that there is a constant probability that an active molecule will decompose chemically. They denote by "A", the probability than an active molecule will decompose within one second.

Their/

Their final formula is

$$k = A \frac{Pa}{Pn} e^{-\frac{Ea - En}{RT}}$$

-Where Pa = a priori probability of the state "a" E_a = energy characteristic of the state "a" and P_n and E_n refer to the normal state. As the ratio $\frac{Pa}{Pn}$ is known to be nearly 1, and (Ea - En) is really what Marcelin called the critical increment we may write

$$k = A e^{-E/RT}, \qquad (e)$$

whence $A = S$.

Now Christiansen & Kramers point out that the molecules formed by the spontaneous chemical change will contain a large amount of energy; for, besides the heat energy liberated by the chemical action, they have the energy of activation. Thus these molecules will be best fitted to activate by collision a fresh molecule of the original substance. The latter, in turn, will decompose and then hand on its energy, in a similar way, to a third inactive molecule. Thus "reaction chains" may be formed.

THE "ACTIVE LIFE".

These authors, then, have succeeded in giving a definite physical meaning to the constant S of equation (c) - namely, "the probability that an active molecule/

molecule will decompose in one second" (A). Expressed in the language of the differential calculus, A is the fractional change in the number of active molecules during the small interval of time δt, divided by that interval of time.

(e) $A = -\frac{\delta C_a}{C_a} \times \frac{1}{\delta t}$ i.e. $-\frac{1}{Ca} \cdot \frac{dCa}{dt} = A$

(Where other methods of change in C_a are ignored)
Now this will be recognised as exactly similar in form to the unimolecular constant for the change - regarded as a whole (Equation (b))

i.e. $k = -\frac{1}{Cn} \cdot \frac{dCn}{dt}$, where "n" refers to the normal molecules.

A may be regarded as the "fragility" of the active molecules - to borrow an expression from Perrin.
Now we know that $1/k$ is the "average life" of a molecule in a unimolecular change, just as $1/\lambda$ is the average life of the radioactive species, which is disintegrating according to the law,

$$\frac{1}{t} \log \frac{N_o}{N} = \lambda \quad (\text{or } \lambda = -\frac{1}{N} \frac{dN}{dt})$$

(For the proof of this see Rutherford "Radio active Substances" (1912) p.419).
For this reason we see, that $1/A$, as defined above, must be the <u>average life of an active molecule</u>.

Christiansen and Kramers, however, find the anomaly that the time of duration of a collision (as estimated by kinetic theory $\sim 10^{-13}$ sec.) is greater than/

than the average active life, (10^{-14} sec) as obtained from experiment. In such a case it would seem that, generally speaking, there will be little chance for a molecule to be deactivated by a second collision. Thus, they conclude, a reversible interchange by collisions, between active and inactive molecules is a misleading conception of the mechanism of reaction and the idea of "active molecules" loses its physical significance.

Now the "duration of a collision" is an arbitrary quantity - a rough estimate of the time taken by the most violent part of the encounter. Further, the value used by Christiansen and Kramers (10^{-13} sec) is an average which applies, therefore, to the collisions between normal molecules. On the other hand, the collisions which lead to activation are abnormally violent. In these cases, the molecules will approach and recede from one another with greater relative velocity than usual, and from this general consideration, it is obvious that the time of such a collision will be smaller than 10^{-13} sec.. This expectation is borne out by dynamical treatment, as the approximate formula for the duration of a half collision is given by Jeans (Dyn. theory of gases, 2nd Edition, p.371) as $\frac{10^{-8}}{V}$ secs., where V is the relative velocity of the two molecules before the encounter.

If we assume with Christiansen and Kramers that the energy of activation is derived from the kinetic energy of/

of the colliding molecules, before impact, then this total K.E. will be $Q + 2q$, where Q is the energy of activation, and q is the average kinetic energy of a molecule.

If v is their relative velocity and m their mass

$$\tfrac{1}{2} mv^2 \geq Q + 2q .$$

$Nq = \frac{3RT}{2}$, at $45^{\circ}C$ = 950 cals. per gm. mol.

Using Daniel's and Johnston's results:

NQ = 24,700 cals , Nm (N_2O_5) = 108.

i.e. $$v^2 \geq \frac{2 \times 26{,}600 \times 4.2 \times 10^7}{108} \geq 2.1 \times 10^{10}$$

i.e. $V \geq \sqrt{2} \times 10^5$ cm./sec

- the relative velocity of two molecules before an activating collision.

Hence time of an activating collision $\leq$

$$\frac{10^{-8}}{\sqrt{2} \times 10^{+5}} \leq 7 \times 10^{-14} \text{ secs.}$$

Thus the use of Jeans' formula shows, contrary to what we might have expected, that the duration of such a collision is very little less than a normal one.

At $45^{\circ}C$. for D. & J's results:

$A = 6.4 \times 10^{13}$ i.e. $\frac{1}{A}$ (the life of an active molecule) $= 1.5 \times 10^{-14}$ secs.

In view of the roughness of these calculations, we can say, that the <u>maximum</u> duration of an activating collision is of <u>the same order of magnitude</u> as the "active life". However the former duration may and will/

will have smaller values-when deactivation by collision will be quite possible. Christiansen's and Kramer's difficulty thus disappears.

The case for the existence of "active molecules", will be seen from the above, to be fairly well established and all the more so, since the introduction of the theory of stationary states. Now, Arrhenius originally supposed that the active molecules would be in simple equilibrium with the inactive molecules, i.e. If C_a = No. of active molecules (a) per cc. and C_n = No. of normal (n) molecules per cc.

$$(1) \quad \frac{Ca}{Cn} = \text{Const.} = \alpha$$

- the ratio α being very small.

The a molecules differ from the n molecules, primarily in the amount of energy they contain and we may suppose them to acquire that energy by collision with other molecules. In the case of unimolecular decomposition, as has been mentioned, the molecules (a') formed by dissociation (from the active molecules) will be very energetic and, therefore, mainly instrumental in activation. If this mechanism overpowers all others, then the concentration of a molecules will be determined by the product of the NO. of n molecules and the NO. of a' molecules present:

$$\text{i.e.} \quad (2) \quad C_a = \alpha' \, C_n \, C_{a'}$$

It is the purpose of the following to examine, how far each of these equations (1 and 2) is compatible with/

with obedience to the unimolecular law.

$$\text{i.e.} \quad -\frac{1}{C_n} \cdot \frac{dC_n}{dt} = k \quad \text{(const.)}$$

I. ARRHENIUS EQUILIBRIUM.

The assumption, we have made for the process of reaction, may be represented -

$$n \rightleftharpoons a \longrightarrow a' .$$

The change $\underline{a} \longrightarrow \underline{a}'$ is assumed to take place like a radioactive or unimolecular one. i.e. No. of molecules of $\underline{a}$ dissociating per sec. $= A\, C_a$, where A has the meaning given by Christiansen and Kramers. No assumption is made as to the change $\underline{a}' \longrightarrow \underline{n}'$ - the deactivation of the products.

Now $\underline{a}$ molecules can change only to $\underline{a}'$ or to $\underline{n}$ molecules. We may therefore say: the rate of decrease of $\underline{n}$ molecules = rate of increase of $\underline{a}$ molecules + rate at which $\underline{a}$ molecules decompose spontaneously to give $\underline{a}'$ molecules.

$$\text{i.e.} \quad -\frac{dC_n}{dt} = \frac{dC_a}{dt} + A\, C_a \qquad (3)$$

But from (1) $\quad C_a = \alpha C_n$

$$\text{i.e.} \quad \frac{dC_a}{dt} = \alpha \frac{dC_n}{dt}$$

$$\text{i.e.} \quad -\frac{dC_n}{dt} = \alpha \frac{dC_n}{dt} + A \alpha C_n$$

$$\text{i.e.} \quad -\frac{dC_n}{dt}(1 + \alpha) = \alpha A C_n$$

$$\text{i.e.} \quad -\frac{1}{C_n} \cdot \frac{dC_n}{dt} = \frac{\alpha A}{1 + \alpha} \qquad (4) \qquad = \text{Constant at constant temp.}$$

Instead of the simple assumption (1) C. & K. deduce from the thoery of stationary states

$$\frac{Ca}{Cn} = \frac{Pa}{Pn} e^{-\frac{Ea - En}{RT}} \qquad (5)$$

when Pa, Pn are a priori probabilities of the a th and n th states, i.e.

$\alpha = \frac{Pa}{Pn} e^{-\frac{Ea - En}{RT}}$ - a constant at constant temperature.

From (4) then the unimolecular constant,

$$k = -\frac{1}{Cn} \cdot \frac{dCn}{dt} = \frac{A \frac{Pa}{Pn} \times e^{-\frac{(Ea - En)}{RT}}}{1 + \frac{Pa}{Pn} e^{-\frac{(Ea - En)}{RT}}}$$

and since α is very small,

$$k = A \frac{Pa}{Pn} e^{-\frac{(Ea - En)}{RT}} . \qquad (6)$$

This is C. & K.'s formula and the importance of the above is that this formula is shown to follow inevitably from the three assumptions:

(1) Arrhenius equilibrium between active and inactive molecules.

(2) Constant probability that an active molecule will decompose spontaneously.

(3) Establishment of equilibrium between a and n much more rapid than the spontaneous decomposition of a.

Under these conditions, the method by which the activated products lose their energy can have no influence/

influence on the constant measured, and the question of reaction chains does not arise.

It is of interest to estimate the relative proportion of active molecules. From (4).

$$\alpha A = k \quad \text{i.e.} \quad \alpha = \frac{k}{A} = \frac{10^{-4}}{10^{14}} = 10^{-18} .$$

II. REACTION CHAINS:

If now we suppose the concentration of active molecules to be governed by equation (2), two cases will arise according as we assume the deactivation of the products to be reversible or irreversible.

(a) Let us assume, first, that this process is reversible, i.e. mass-action equilibrium between $\underline{a}'$ and $\underline{n}'$. Then our picture of the reaction is:-

$$n\ (+\ a') \rightleftharpoons a \longrightarrow a' \rightleftharpoons n' .$$

Then $C_{a'} = \beta\, C_{n'}$ (7) where β is small.

As before $-\frac{dCn}{dt} = \frac{dCa}{dt} + A\, C_a$ (3)

And applying the same idea to the $\underline{a}'$ molecules,

$$\frac{dCn'}{dt} = A\, C_a - \frac{dCa'}{dt} \qquad (8)$$

Finally $Ca = \alpha'\ Cn\ Ca'$ (2)

- the initial assumption.

Differentiate (7) and (2) with regard to $\underline{t}$,

$$\frac{dCa'}{dt} = \beta \frac{dCn'}{dt} \qquad (9)$$

$$\frac{dCa}{dt} = \alpha'\ Cn \frac{dCa'}{dt} - \alpha'\ Ca' . \frac{dCn}{dt} \qquad (10)$$

Using (9) with (8) (11)

$$\frac{1}{\beta}\cdot\frac{dCa'}{dt} = A\,Ca - \frac{dCa'}{dt} \quad \text{i.e.} \quad \frac{dCa'}{dt} = \frac{A\,Ca}{1+\frac{1}{\beta}} = \frac{\beta A\,Ca}{1+\beta}$$

Substitute (2) and (11) in (10),

$$\frac{dCa}{dt} = \alpha' Cn \frac{\beta A\,Ca}{1+\beta} + \frac{Ca}{Cn}\cdot\frac{d\,Cn}{dt} \qquad (12)$$

Substitute value of $\frac{dCa}{dt}$ from (3)

$$-\frac{dCn}{dt} - A\,C_a = \frac{\alpha'\beta A}{1+\beta}\,Ca.Cn + \frac{Ca}{Cn}\cdot\frac{dCn}{dt}$$

$$\text{i.e.} \quad \frac{dCn}{dt} = -\frac{A\,Ca - \frac{\alpha'\beta A}{1+\beta}\,Ca\,Cn}{1+Ca/Cn}$$

Therefore the unimolecular constant k

$$= -\frac{1}{Cn}\cdot\frac{dCn}{dt} = \frac{A\frac{Ca}{Cn} + \frac{\alpha'\beta A\,C_a}{1+\beta}}{1+\frac{Ca}{Cn}}$$

Since the concentration of active molecules (reactants or products) is very small then $\frac{Ca}{Cn}$ and β are small in comparison with 1.

$$\text{i.e.} \quad k = A\,\frac{Ca}{Cn} + \alpha'\beta A\,Ca = A\,\alpha'\,(C_a' + \beta\,C_a) \qquad (13)$$

Now if Ca and C_a' are of the same order of magnitude (as we should expect)

$$k = A\,\alpha'\,C_{a'} = A\,\alpha'\beta\,C_{n'}$$

Thus the unimolecular constant is directly proportional to the concentration (C_n') of the molecules formed by the change, i.e. An <u>autocatalytic</u> reaction will be found - where the velocity constant is of the form:

$$k' = \frac{1}{C_n C_{n'}} \cdot \frac{dCn}{dt} \quad \text{or} \quad \frac{dCn}{dt} = k' (C_o - C_n) C_n \ .$$

The condition then,on which such a type of reaction will give a unimolecular constant is $C_{n'}$ = const. Or $C_{a'}$ = Const. and from equation (2) we see that this is equivalent to Arrhenius equilibrium: C_a = Const. x Cn.

(b) In the second place we may assume the deactivation to take place irreversibly.

$$n \rightleftharpoons a \longrightarrow a' \longrightarrow n'$$

The equations are then:

$$Ca = \alpha C_n C_{a'} \qquad (2)$$

$$- \frac{dCn}{dt} = \frac{dCa}{dt} + A C_a \qquad (3)$$

$$- \frac{dC_{a'}}{dt} = B C_{a'} - A C_a \qquad (14)$$

Where a' is supposed to decompose spontaneously and unimolecularly with velocity B.

Differentiate (2) as before, then,

$$\frac{dCa}{dt} = \alpha Cn \frac{dCa'}{dt} + \alpha C_{a'} \cdot \frac{dCn}{dt} \qquad (10)$$

$$\text{i.e.} \quad - \frac{dCn}{dt} - A\ Ca = \alpha C_n (-B\ C_{a'} + A\ C_a) + \alpha C_{a'} \frac{dCn}{dt}$$

$$\text{i.e.} \quad \frac{dCn}{dt} (1 + \alpha C_{a'}) = -A\ Ca + \alpha B C_n C_{a'} - \alpha A\ C_n C_a$$

$$= - A \alpha C_n C_{a'} + \alpha B\ C_n C_{a'} - \alpha^2 A\ C_n^2 C_{a'}$$

$$\text{i.e. } \frac{1}{C_n} \cdot \frac{dC_n}{dt} = \frac{\alpha C_{a'} (- A + B - \alpha A\, C_n)}{1 + \alpha C_{a'}}$$

The problem is, to find the conditions under which this expression will be constant.

If the change $\underline{a} \longrightarrow \underline{a}'$ is much quicker than $a' \longrightarrow \underline{n}'$ then $\frac{C_a}{C_{a'}}$ and $\therefore$ (αC_n) will be small in comparison with 1.

We already know $\alpha C_{a'} = \frac{C_a}{C_n}$ is small in comparison with 1.

Hence $k = - \frac{1}{C_n} \frac{dC_n}{dt} = \alpha C_{a'} (A - B) = \alpha C_{a'} A$.
(since A is much greater than B, by the above assumption.)

The $\underline{a}'$ molecules are in the same position as an element in a radioactive series and therefore when the reaction is proceeding steadily, $C_{a'}$ will become constant and the change will follow the unimolecular law. Again, however, by relation (2) this will lead to Arrhenius equilibrium between the active and inactive molecules. $\frac{C_a}{C_n} = \alpha C_{a'} =$ constant.

Now in this case we have assumed that the change $\underline{a}' \longrightarrow \underline{n}'$ is slower than $\underline{a} \longrightarrow \underline{a}'$, which, in turn, we have already assumed much slower than $\underline{n} \longrightarrow \underline{a}$ or $\underline{a} \longrightarrow \underline{n}$. Thus the deactivation of the active product is required to be very much slower than the deactivation of the active reactant - processes which are very probably similar in nature. The mechanism of II(b) is therefore highly improbable.

CONCLUSION.

Summing up the second part of this investigation, we can say, that, if the energy of activation is acquired at the expense of the highly energised reaction products, then the reaction will follow the simple unimolecular law only, when the conditions are such, that there is simple proportionality between the concentrations of active and inactive molecules. (a) If the deactivation of the active products takes place reversibly, the reaction will be autocatalytic in general. (b) When this deactivation is a spontaneous irreversible change, then the law will be unimolecular if this deactivation is much slower than the loss of energy by the active reactant.

It thus appears that the tentative suggestion made by Arrhenius in 1889 (Zeit. f. Phys. Chem. 4, 226) is justified; namely, that a simple equilibrium between active and normal molecules is characteristic of unimolecular reaction. A reaction chain mechanism, on the other hand, leads to an auto-catalytic process. That the second type can be so modified as to lead to the first, is shown in part (I) of this work.

SUMMARY.

PART I.

CARBON MONOXIDE DECOMPOSITION OF OXALACETIC ESTER DERIVATIVES.

1. The thermal dissociation of ethoxy-oxalacetic ester, oxalpropionic ester and oxalsuccinic ester is found to follow the unimolecular law, at temperatures between 140°C and 200°C.

   COOEt.CO. CHR. COOEt $\longrightarrow$ CO + COOEt. CHR. COOEt

2. The loss of carbon monoxide by the parent-substance - oxalacetic ester - is also unimolecular, though accompanied by a condensation-reaction.

3. The reaction is unaffected by solvents and hydrogen ion, but is retarded by an excess of carbon monoxide. When this gas is allowed to escape under its own pressure, the change is still of the first order.

4. The velocity varies with temperature according to the Arrhenius law. In the integrated equation;

$$\log_{10} K = - \frac{Q}{2.3\,RT} + B$$

the values of Q and B with different compounds, are roughly proportional.

- R	- OEt	- CH_3	- CH_2COOEt	- C_6H_5
Q	35,800	33,300	35,400	44,300
B	13.9	13.4	14.3	19.9

These constants have similar values in other unimolecular changes.

5. No evidence can be obtained in favour of the Lewis-Perrin radiation theory, either from absorption-spectra or by illumination.

6. The decomposition of phenyl-oxalacetic ester is autocatalytic, following the equation:

$$\frac{dx}{dt} = k\,(a-x)x \quad .$$

7. The change probably proceeds by reaction-chains.

PART II.

THE THEORY OF THE UNIMOLECULAR REACTION.

1. The hypothesis of Lewis and Perrin of activation by radiation in thermal reactions, is shown to have very little theoretical foundation.

2. The experimental values of the "life of an active molecule" (A) in the equation,

$$k = A\, e^{-Q/RT}$$

are shown to be not incompatible with activation by collision.

3. This equation is a particular case of the more general one:

$$k = \frac{\alpha A}{1 + \alpha} \quad ,$$

where α is the constant of the equilibrium between active and normal molecules.

4. If we assume that (a) the rate of formation of active molecules is great in comparison with their rate of chemical reaction and that (b) there is a constant probability that an active molecule will react, then the law of change will be unimolecular only when, as Arrhenius supposed, there is simple proportionality between the concentrations of active and normal molecules.

5. If the active product of the reaction hands back its energy, by collision, to a second reacting molecule the change will most probably be auto-catalytic.
